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SIMULTANEOUS ARGON DIFFUSION AND ELECTRICAL CONDUCTION
MEASUREMENTS IN MICROCLINE FELDSPAR

by

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
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EDMONTON, ALBERTA

APRIL, 1966

UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled SIMULTANEOUS ARGON DIFFUSION AND ELECTRICAL CONDUCTION MEASUREMENTS IN MICROCLINE FELDSPAR, submitted by Peter Paul Pronko in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

A study has been made on the feasibility of measuring simultaneously the diffusion of gas in a solid and the electrical conduction of mobile ions in that solid. The method employs an analysis of dynamic flux-time data taken for the diffusion of gas and the current of ions in the material.

This procedure has been applied to the study of argon diffusion and ionic conduction in microcline feldspar. Transitions in the diffusion and conduction properties have been correlated with a possible disordering phenomena in microcline. The simultaneous data suggest that a model which employs "trapping" of argon atoms in vacancies (caused by the disordering) can be used to explain the character of argon retention in this material.

Analysis of the flux-time curves indicates that a relatively large diffusion coefficient ($D \sim 10^{-8} \text{ cm}^2/\text{sec}$), exists for the movement of argon in microcline feldspar at low temperatures ($T \leq 350^\circ \text{ C}$) and this has associated with it a low activation energy of $\sim 3 \text{ K Cal/mole}$ (.13 e.v.). For higher temperatures ($> 500^\circ \text{ C}$), the activation energy increases to $\sim 35 \text{ K Cal/mole}$. Pronounced trapping at the higher temperatures may be responsible for decreasing the diffusion coefficient by several orders of magnitude. The nature of these trapping

sites may be studied by means of electric field induced ionic collisions with the argon atoms. Evidence is presented for a quantum character in the energy states associated with the trapped argon. The implication of this quantum trapping on the diffusion properties of argon is discussed and an explanation of the observed character of argon retention in feldspars (as well as other minerals) is proposed on the basis of trapping in vacancy defects.

ACKNOWLEDGMENTS

The ideas and opinions contained within this dissertation have developed over a period of several years. They are an outgrowth of discussions with various individuals, some of whom were closely associated with the subject and others who, though interested, were less directly involved. They have all in their own way contributed to the final results of the study.

Thanks are extended to Dr. H. R. Krouse for his encouragement and advice as supervisor of the research.

The technical assistance of Mr. H. McCullough, which was extremely helpful in the initial stages of the experimental work, is gratefully acknowledged.

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It is appropriate to mention Dr. J. Lipson of the University of Pittsburgh who originally introduced me to this subject and the problems associated with it. I also wish to extend my gratitude to Dr. H. Glyde of the University of Sussex who directed my attention to the possibility of a trapping phenomena.

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INTRODUCTION

The primary purpose of this research is the evaluation of an experimental method which studies gas diffusion from a solid while allowing for the simultaneous application of an electric field throughout the solid. These experimental conditions result in a determination of the effect which an electric field has on the gas diffusion properties and can produce, if required, measurements of electrical conductivity in the solid.

This thesis describes measurements of argon diffusion and its modification by an electric field in the mineral microcline feldspar. Since feldspar becomes an ionic conductor at a few hundred degrees above room temperature, the investigation reduces to a study of the ionic and atomic movements in this mineral and their mutual interactions. Additional motivation for the study is associated with the use of the mineral feldspar (KAlSi_3O_8) in making geologic age determinations by the K^{40} - Ar^{40} method. K^{40} decays to Ar^{40} through electron capture with a half life of 1.18×10^{10} years. Information concerning the diffusion of argon in K-feldspar will be of interest to workers in the fields of geochronology and mineralogy.

E. K. Gerling et al (1954) made some of the first attempts to study diffusion of argon from minerals. They attempted to observe Ar diffusion properties by monitoring the

dynamic flux-time gas release with a mass spectrometer. Their method of analysis is only valid for asymptotically large values of time (or very large diffusion coefficients) and is at best only an approximate way of determining activation energies over the temperature intervals 100°C. to 1000°C. Their approach to the problem is to obtain a solution for the diffusion equation by means of separation of variables (Crank 1959) and to express the concentration of diffusing substance at any time with an infinite series of the following form:

$$\frac{C_o - C}{C_o} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \pi^2 Dt/a^2) \quad (1.)$$

" C_o " is the concentration before starting the diffusion anneal, " C " is the concentration after a time " t ", " D " is the diffusion coefficient, and " a " the radius of the crystal grain from which diffusion is being studied. The initial concentration is assumed to be uniform throughout the crystal. If Dt/a^2 is sufficiently large (≥ 0.1) only the first term of the infinite series is used. Gerling (1962) used the time rate of change of concentration as a measure of the rate of gas release. This was expressed as $\frac{dC}{dt} = A \exp(-KDt/a^2)$ and was used to analyze the flux rate of gas monitored with a mass spectrometer. Observing the change in KD/a^2 with

temperature gave Gerling's estimates of the activation energy. Gerling's method is only approximate and will generally be completely invalid for small diffusion coefficients. His method has been criticized by Brandt (1962) who showed that the results are only valid if $\pi^2 Dt/4a^2 > 1$. This requirement is seldom met in the temperature intervals studied by Gerling and co-workers. A review of Gerling's work may be found in *Geokhimiya*, 1962, no. 12, pp. 1254-1273.

Kh. I. Amirkhanov et al (1961) have extended the method of Gerling by taking into account higher order terms in the series and observing the fraction of gas retained in the sample after a given annealing time. From a mathematical and analytical standpoint their results are more reliable than those of Gerling and co-workers, but their experimental points are separated by time intervals of 1/2 hour or more. This is a necessary requirement if significant fractional change in concentration is to occur. Time intervals of this magnitude eliminate the possibility of following detailed changes in the experimental curves and result in a mean value for the diffusion coefficient. This method also eliminates the possibility of studying detailed diffusion behavior in the first half hour of the anneal.

Variations on the method of Amirkhanov et al (1961) have appeared at various times in the literature (Booth 1957, Glyde and Mayne 1965, Gentner et al 1960). These workers have used either radioactive counting or mass spectrometer monitoring to determine fractional changes in the concentration of diffusing substances. Their diffusion coefficients are calculated from equations of the form

$$\frac{C_o - C}{C_o} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \pi^2 Dt/a^2)$$

or its low diffusion coefficient approximation of

$$\frac{C_o - C}{C_o} = \frac{6}{\pi^{1/2}} \left(\frac{Dt}{a^2}\right)^{1/2} - \frac{3}{a^2} Dt \quad (2.)$$

$\frac{C_o - C}{C_o}$ is the fractional release of gas in a time period t .

This analytical approach is valid and experimentally accurate; however, it tends to integrate results by requiring relatively large values of time and supplies no way of studying grain boundary or dislocation diffusion. This latter condition arises because of the use of C_o , the total concentration, in determining diffusion coefficients. Dislocation diffusion would most probably appear as a very rapidly decaying burst of diffusing substance (due to a large diffusion

coefficient), and would represent only a small fraction of the total gas content of the material. Since a small change in concentration would occur from this, equation (1.) or (2.) would result in an incorrectly small diffusion coefficient. It is for this reason that an attempt has been made in this thesis to establish an analytical method which can in some way rely on the curvature of the flux-time decay curve to produce a diffusion coefficient. A suitably discriminating procedure should allow for a differentiation between the two components of body diffusion and dislocation diffusion. A method of flux-time curve fitting between theoretical and experimental points should supply this necessary result. This method is also desirable in that it supplies information in regions of both small and large time.

Various flux-time equations are discussed in the present work and their ability to meet the requirements outlined above is evaluated. In arriving at the desired equations one must come to a decision about the geometry of the sample. Spherical geometry was used in all previous investigations of argon diffusion from feldspar crystals. The sample preparation used by previous workers usually consisted of crushing the material into small granules a fraction of a millimeter in radius. Large gas release is obtained from the crystal when it is in this form due to the large surface area associated with crushed material. Since the feldspar lattice

is highly anisotropic and shows marked directional dependence of ionic conductivity (Pronko 1962) it is felt that diffusion studies should be confined to a single crystal orientation. For this reason a thin plate geometry was chosen in the present work. The bulk of the diffusion is then perpendicular to the faces of the thin plate. The flux time equation for one dimensional diffusion will be equally valid for diffusion along a line, a plane, or from the faces of a thin slab. Grain boundary and dislocation diffusion of argon may possibly be studied using this geometry. Levine and MacCallum (1960) discuss the empirical nature of diffusion along grain boundaries of a polycrystalline body. It is necessary to consider this latter situation since microcline feldspar has a complex network of twin planes, exsolution planes, and cleavage planes which collectively may act as paths for the enhanced diffusion of argon.

The basic microcline feldspar structure (in its idealized form) is a triclinic unit cell of interconnecting Si-O_4 tetrahedra where one out of every four silicon atoms is substituted for by an aluminum atom. These tetrahedra are linked together by potassium ions resulting in a chemical composition of KAlSi_3O_8 for the microcline structure. Such an ideal composition of microcline feldspar cannot be made in the laboratory due to pressure and time considerations. One

is therefore compelled to study the naturally occurring crystal which in reality is quite complex but extremely interesting. When most minerals form in their natural state, they crystallize under conditions which usually permit two or more elements to occupy a given lattice site. In microcline sodium substitutes for potassium and aluminum for silicon. Other substitutional replacements may take place, however they are not as pronounced as these. At temperatures above $\sim 660^{\circ}$ C., complete solid solution exists between $\text{NaAlSi}_3\text{O}_8$ and KAlSi_3O_8 . Below this temperature, "solid solutions" of potassium and sodium feldspar are unstable and under conditions of slow cooling, break down into an oriented intergrowth of subparallel bands alternating between sodium-rich feldspar and potassium-rich feldspar. These alternating bands are observed to repeat themselves along the "a" axis. This condition is referred to as perthitic exsolution and is observable in the crystal being studied. The sample studied is between 70 and 80% potassium-rich feldspar with the remainder being sodium-rich feldspar. The exsolution bands are of triclinic symmetry for both the KAlSi_3O_8 and the $\text{NaAlSi}_3\text{O}_8$. The "a" unit length for potassium feldspar is 8.44 Å and that of sodium feldspar is 8.14 Å, however the "b" and "c" unit lengths are more nearly equal (12.95 Å, 7.15 Å and 12.79 Å, 7.15 Å). It is for this reason that the exsolution bands appear approximately parallel to the (100) plane. The

"b" and "c" lengths coincide in the (100) plane whereas the "a" length is alternately longer for the K-rich bands and shorter for the Na-rich bands. Photomicrographs of the sample under study are shown in figure 1. The photographs (taken with polarized light) show very clearly the exsolution bands. The plane of these photographs is approximately perpendicular to the "c" axis.

In addition to exsolution, the crystal structure is further complicated by crystallographic twinning which is different for the sodic and potassic forms. The process by which these twin structures occur is not fully understood; however they are thought to occur as transformation twins due to readjustment of the lattice in response to deformations. The potassium feldspar has a cross-hatched twinning caused by twin planes intersecting at nearly right angles to each other. This is a microscopic polysynthetic twinning which results in a grid iron lamellae. This grid iron pattern is clearly observable in the photomicrographs taken under polarized light. When the potassium feldspar is found in this heavily twinned form, the crystal system is observed to be triclinic rather than monoclinic. This heavily twinned, triclinic form of potassium feldspar is called microcline.

In like manner, the sodium feldspar is twinned, but only along one direction. The (010) plane acts as the twin plane and striations from this effect are observable on the (001) cleavage. These striations are clearly visible in the photomicrograph and help to delineate the sodic and potassic bands. Further discussion of microcline perthite feldspar may be found in Berry and Mason (1959).

The existence of the above-mentioned crystal defects has prompted many investigators to postulate that radiogenic argon is lost due to rapid diffusion along these structures. This has been supported by the fact that microcline feldspar is observed to lose as much as 40% of its radiogenic argon during geologic time in comparison to other minerals such as mica. At present there is still some confusion over this point. Orthoclase, which is an untwinned pseudo-monoclinic non-perthitic form of K-feldspar, has also been observed to undergo this loss of argon, whereas sanidine (which is a highly disordered monoclinic form of microcline) has not. These facts cause a certain amount of doubt to surround the present thinking that loss of argon from microcline is due solely to its dislocation structure.

One of the principal reasons for studying argon diffusion in microcline perthite feldspar was to determine

whether a defect diffusion mechanism might be observable at temperatures below $\sim 450^{\circ}$ C. Afanas'ev (1960) and Gerling (1960) proposed that radiogenic argon may be lost by migration along the (001) and (010) cleavage cracks and through dislocations caused by "triclinization" of the microcline structure. It is thought that triclinization is a consequence of twinning in microcline. Baadsgaard et al (1959) have proposed that the twin structures may be responsible for the loss of radiogenic argon from feldspar. Rubinshtein (1960) suggests that argon loss takes place along the dislocations associated with the boundaries of the perthitic exsolution veinlets whereas Murina and Sprintsson (1960) claim, on the basis of their diffusion studies, that there is no direct connection between perthitization and argon loss. In addition to this, Pronko (1962) has observed a reduced activation energy for ionic conductivity along directions parallel to twin planes and intersections of twin planes in microcline feldspar. It is obvious from these observations, that a method is required which permits a study of directionally controlled argon diffusion in microcline perthite and other forms of feldspar.

If attention is directed toward body diffusion of argon in feldspar, a similar problem of directional control is encountered. The high degree of anisotropy in the feldspar structure may be seen in the photographs of the unit cell model

of figure 2. The "a" direction is markedly less open than the "b" and "c" directions. Preliminary results of the present study on ionic conductivity indicate that the activation energy for conduction along the "b" and "c" axes is approximately 50% lower than the value for the "a" axis. If one allows for the neutral charge of the argon atom and considers that its chemical bonding to other atoms in the crystal will be of Van der Waals origin, a simple calculation yields a low binding energy of $\sim .15$ e.v. (16 K cal/mole) for the activation energy of diffusion. The unit cell model shows relatively large channels along the "b" and "c" directions and these could afford pathways along which the argon atoms could easily migrate. If this were the case one would expect to observe quite low activation energies corresponding to movement along these channels. It would be difficult to distinguish this experimentally from low activation energies associated with grain boundary diffusion. It is hoped that a method which analyzes detailed flux time curves might allow for a separation of body diffusion from grain boundary and dislocation diffusion. Gentner et al (1960) have experimentally observed low activation energies for diffusion of argon in silicate minerals similar to the one being studied. This low activation energy (~ 7 K cal/mole) is in effect over the temperature interval of approximately 100° C. to 350° C. For higher temperatures, a much larger activation energy is observed (~ 40 K cal/mole).

Other investigators (e.g. Amirkhanov et al 1961) have also observed these large activation energies (~ 35 K cal/mole) for the high temperature diffusion of argon. This suggests that the high temperature diffusion represents migration of argon atoms out of trapping sites, which themselves must be ruptured before the argon is free to diffuse. This concept is developed by Sardarov (1961). He discusses the bonding of argon in a mica lattice and shows that the binding energy is far too small to correspond to the observed large activation energies for diffusion. He then goes on to indicate how the argon atom may become trapped in the planes between the mica layers and concludes that the only way for argon to diffuse out of this trapped position is for the ionic bonds of the crystal lattice to begin dissociating. This concept is further supported in that argon is experimentally observed to remain in the mica lattice until the temperature is high enough to release the structural OH^- as H_2O . This corresponds to a condition of disruption of the crystalline lattice.

Since the argon atoms are electrically neutral, they supply no strong cohesive forces within the solid and consequently cause a strain condition which depends on the atom's size and position. Rimmer and Cottrell (1957) have presented a theoretical discussion of the strain energy associated

with an inert gas atom in the lattice of copper. They find that a large strain energy exists (~ 10 e.v.) when inert atoms are present either substitutionally or interstitially. When in a substitutional position, the strain will come from lack of strong cohesive forces plus the difference in atomic size. However, interstitial presence causes strain which is due principally to size. These authors have proposed that this situation will favor the capturing of vacancies by inert atoms which results in their being trapped.

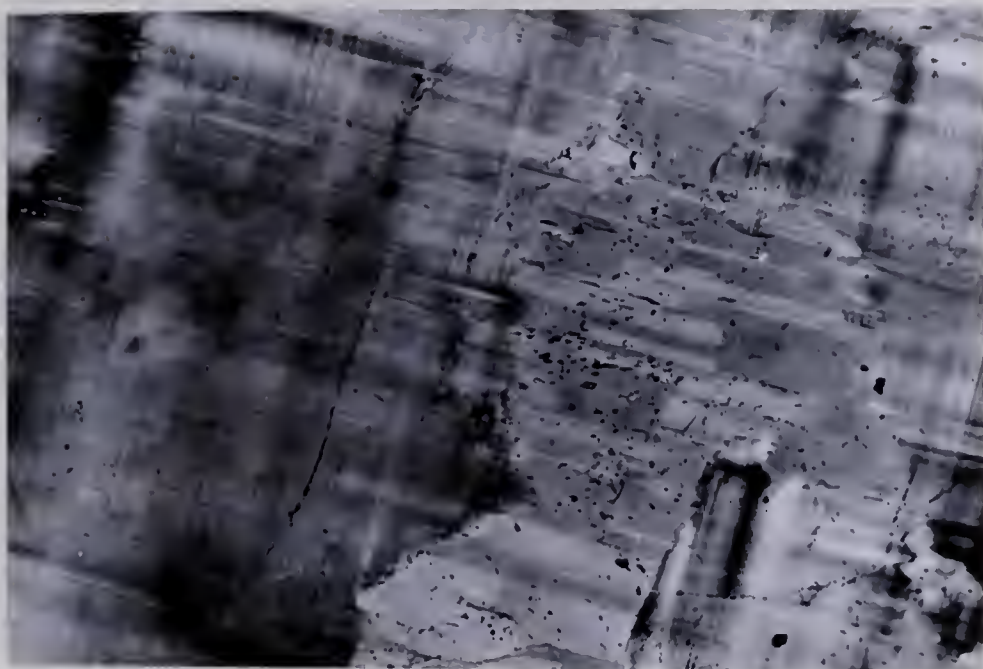
It has been pointed out by Kelly and Ruedl (1966) that the study of inert gas diffusion in solids is often complicated by effects due to oxide skins (Booth and Rymer, 1958), vaporization, phase changes, and various forms of "weak trapping." The first two effects involving oxide skins and vaporization will probably not be encountered in microcline. However, phase changes have been observed in feldspars by Amirkhanov (1961) and these, along with lower temperature transitions have been observed in the present study. These transformations have an observable effect on the behavior of argon diffusion. One apparent result of the transformation is a large increase in ionic conductivity (which indicates the presence of vacancies). It is possible for these point defects to take part in the process defined by Kelly and Ruedl (1966) as "weak trapping."

According to these authors, this phenomenon may include gas-dislocation interaction (Greenwood et al 1959), gas-vacancy-cluster interactions (Lagerwall 1964), the formation of small bubbles with mobilities similar to or less than that of single gas atoms (Ruedl and Kelly 1965) and the formation of bubbles which redissolve at high temperatures (Reynolds 1965).

The process of bubble formation is associated with the condition of supersaturation by the inert gas. The effects of this supersaturation have been discussed by Barnes et al (1963, 1964). A supersaturated solid will exhibit the formation of inert gas bubbles when the temperature is sufficiently high. These bubbles may be observed with an electron microscope and their movements and growth rate determined. The diffusion of these bubbles is not controlled by Fick's laws, but rather is a function of their size and the material in which they reside. The controlling factors on the rate of movement have been developed by Barnes (1964) and depends on such things as thermal gradients and surface diffusion of the material around the bubble. No attempts to date have been made to observe the possible presence of such bubbles of radiogenic argon in minerals. Barnes (private communication) has suggested that the concentration of radiogenic argon in microcline is probably too small for bubble formation to occur, however there is a distinct possibility

that atomic trapping could take place. The concentration of argon in the material being studied in the present work is 3.4×10^{16} atoms/cc. Glyde and Mayne (1965) have studied helium diffusion in aluminum where the helium concentration was 10^{14} atoms/cc. Their results suggest that trapping effects occur within the first five minutes of the diffusion anneal and attribute this to the interaction of helium atoms with clusters of vacancies.

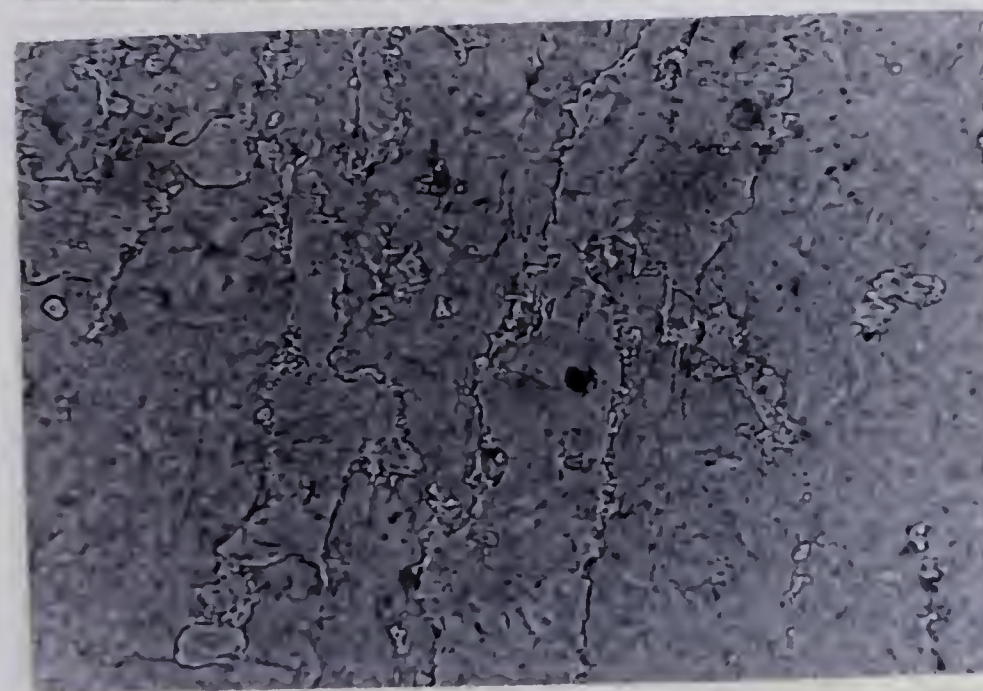
Hurst (1962) has mathematically taken into account the effects of a trapping phenomena on the gas release curves obtained in diffusion of xenon from UO_2 . His results indicate that it is possible for the trapping effects to influence the gas release curves, and in order to explain the complete curve it is necessary to take into account the return of atoms from trapping sites. The return of atoms from trapping sites may occur with a single activation energy, or as pointed out by Murin et al (1962) there may be a spectrum of activation energies.



Polarized Light
x 160

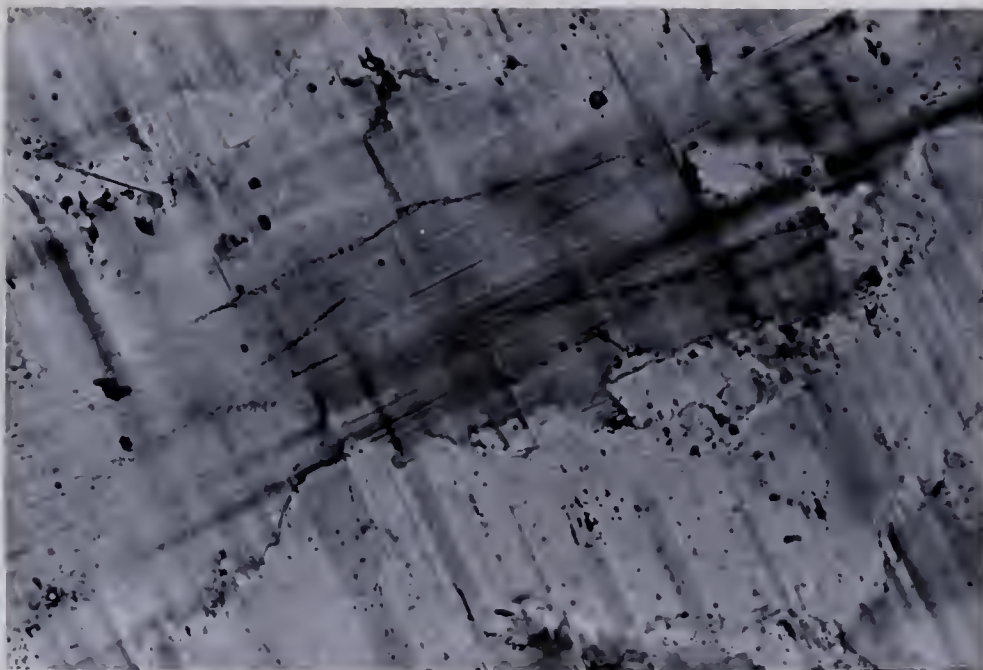


Polarized Light
x 62.5

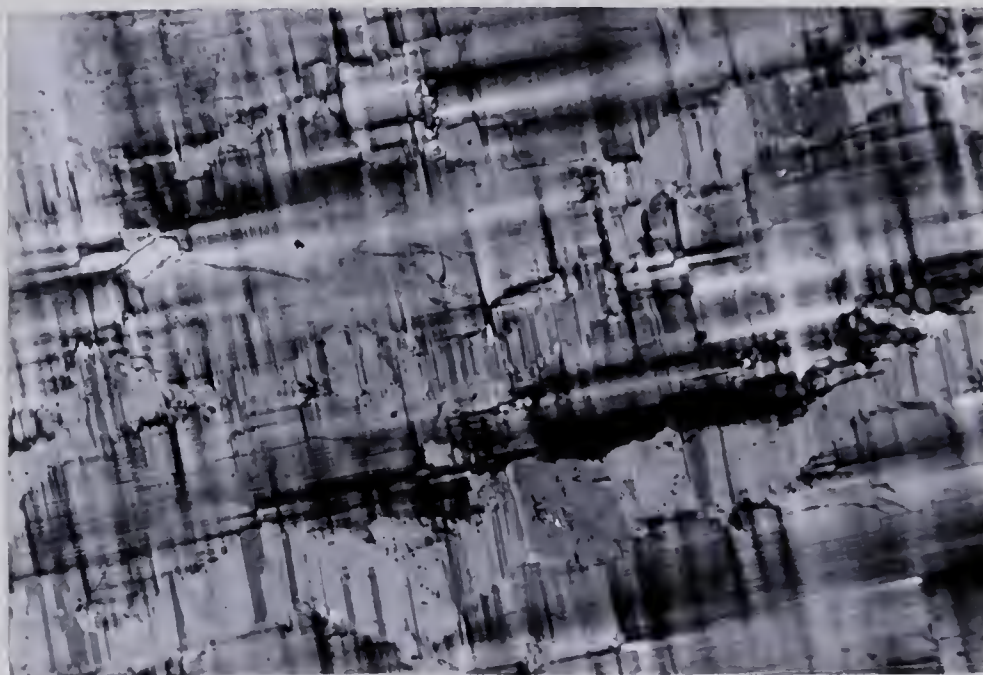


Unpolarized Light
x 62.5

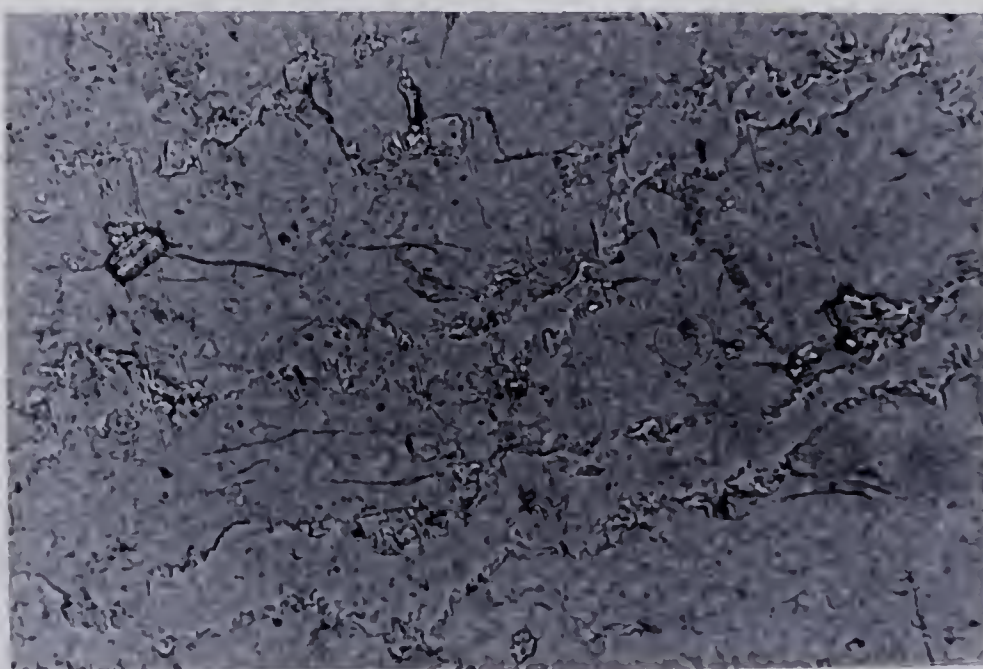
Figure 1A. Photomicrographs of Microcline Perthite



Polarized Light
x 160

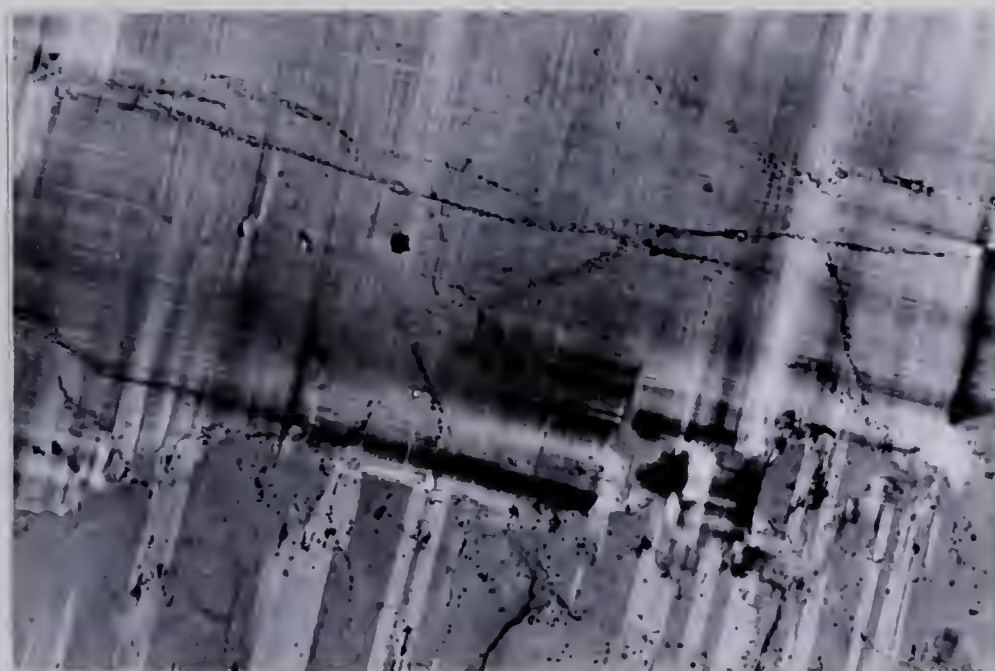


Polarized Light
x 62.5

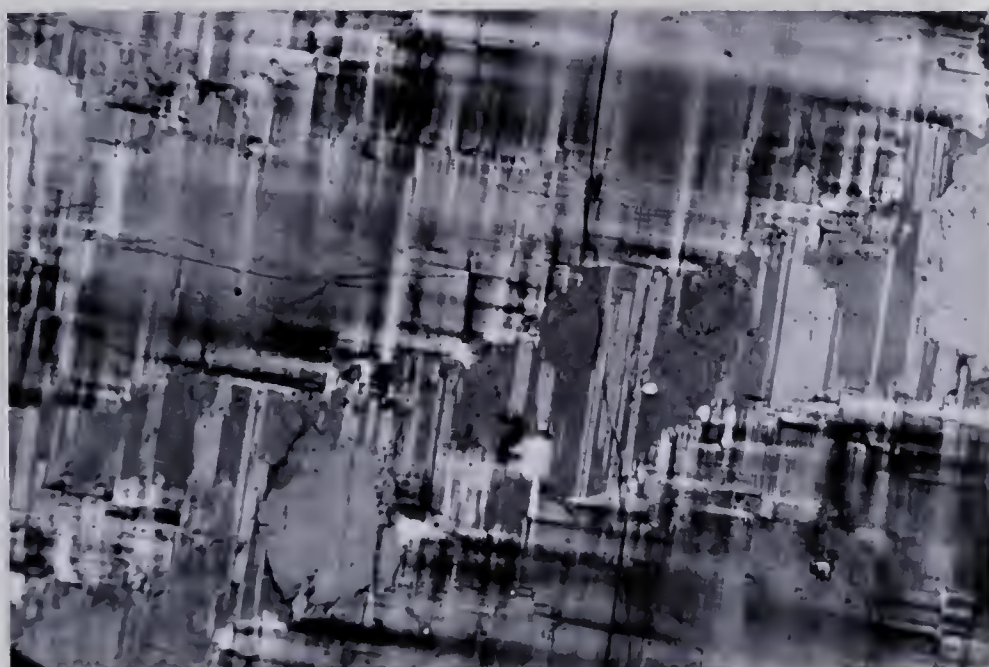


Unpolarized Light
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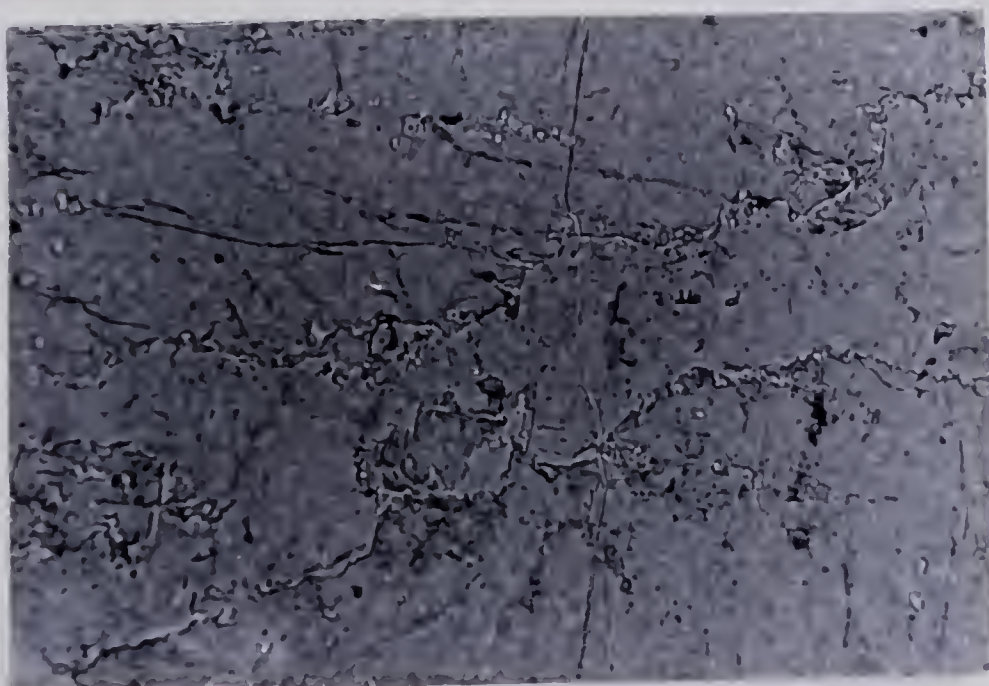
Figure 1B. Microcline Perthite Quenched from ~ 24 Hours
Anneal at 550° C. (Photomicrograph)



Polarized Light
x 160

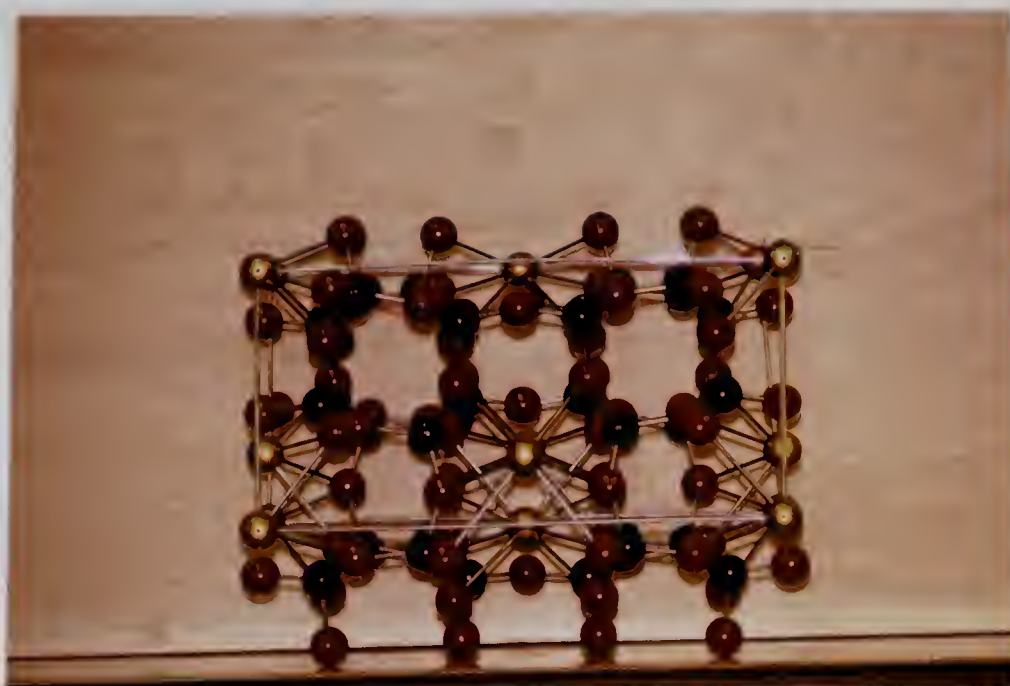


Polarized Light
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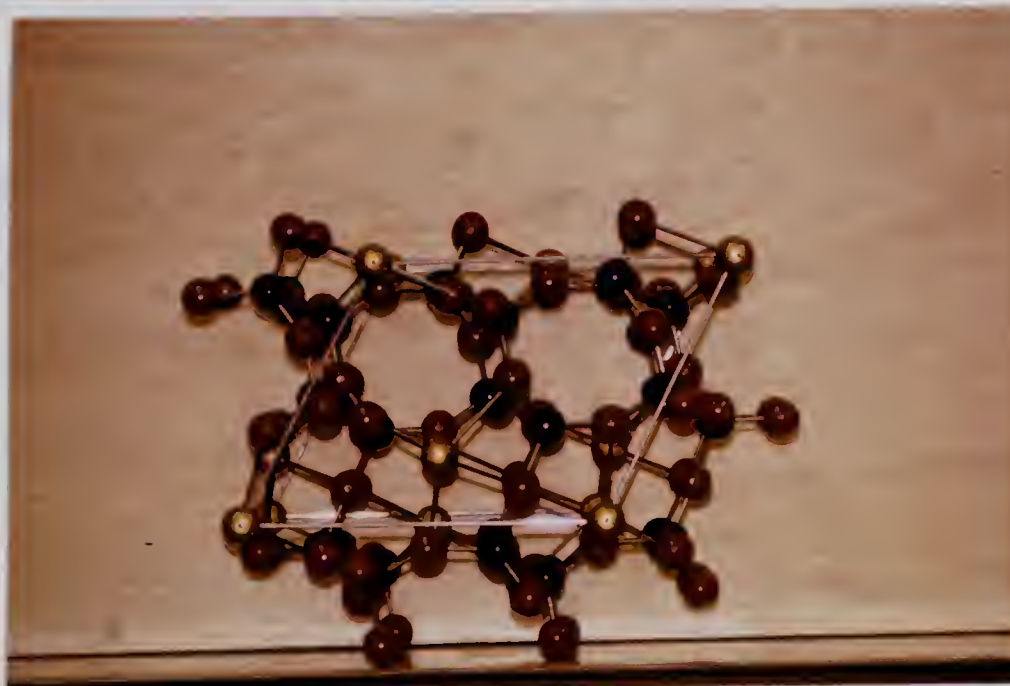


Unpolarized Light
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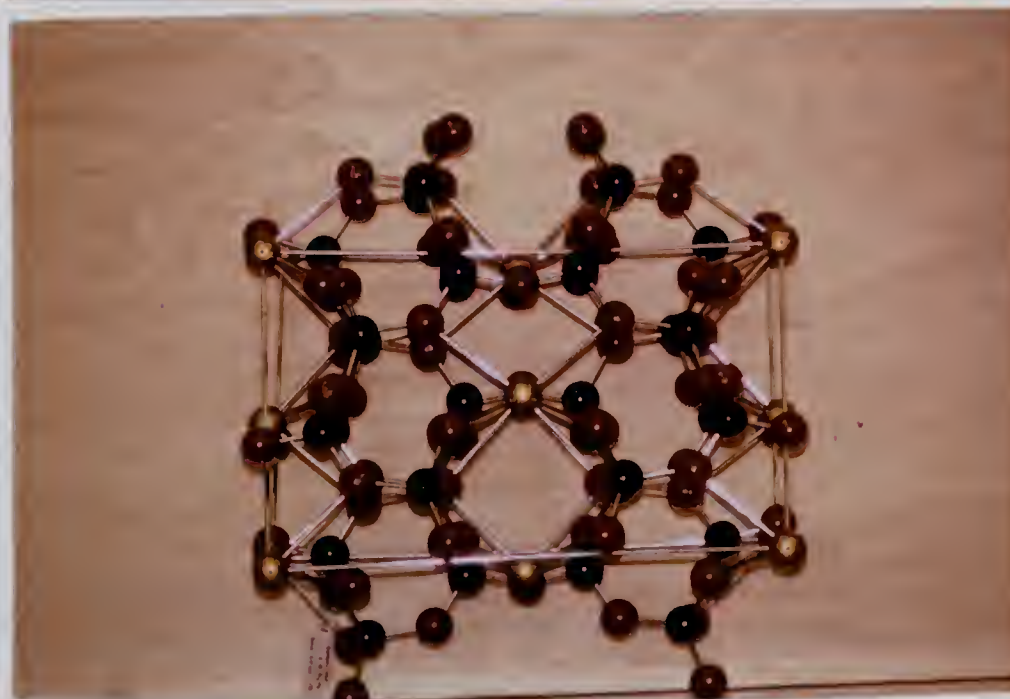
Figure 1C. Microcline Perthite Quenched from ~ 24 Hours
Anneal at 550° C. (Photomicrograph)



[100] direction



[010] direction



[001] direction

Figure 2. Photographs of Feldspar Unit Cell Model.

I. APPARATUS FOR THE SIMULTANEOUS OBSERVATION OF ELECTRICAL CONDUCTION AND GAS DIFFUSION IN SOLIDS

Figure I-1 is a schematic drawing of the diffusion conductivity cell used in these experiments. A key is supplied to indicate the material used for various sections of the cell.

The portion of the cell which is heated was made of high resistivity quartz to minimize alternative paths for electrical conduction. Cooling jackets above and below the furnace, keep this conduction to a negligible value. All metal to glass junctions were made through kovar seals and graded transitions of pyrex were used to connect the quartz to the kovar.

The crystal sample is loaded between the electrodes and its temperature is monitored by an alumel-chromel thermocouple, which is located immediately adjacent to the crystal slab, but not touching it. The electrical resistance of the sample can be measured using a range of applied voltages from 0 to 1000 volts. The temperature of the oven is thermostatically controlled to within $\pm 1.5^{\circ}$ C. using an Assembly Products Inc. Pyrometer Optical Meter Relay and Control Module. Two thermocouples connected in parallel,

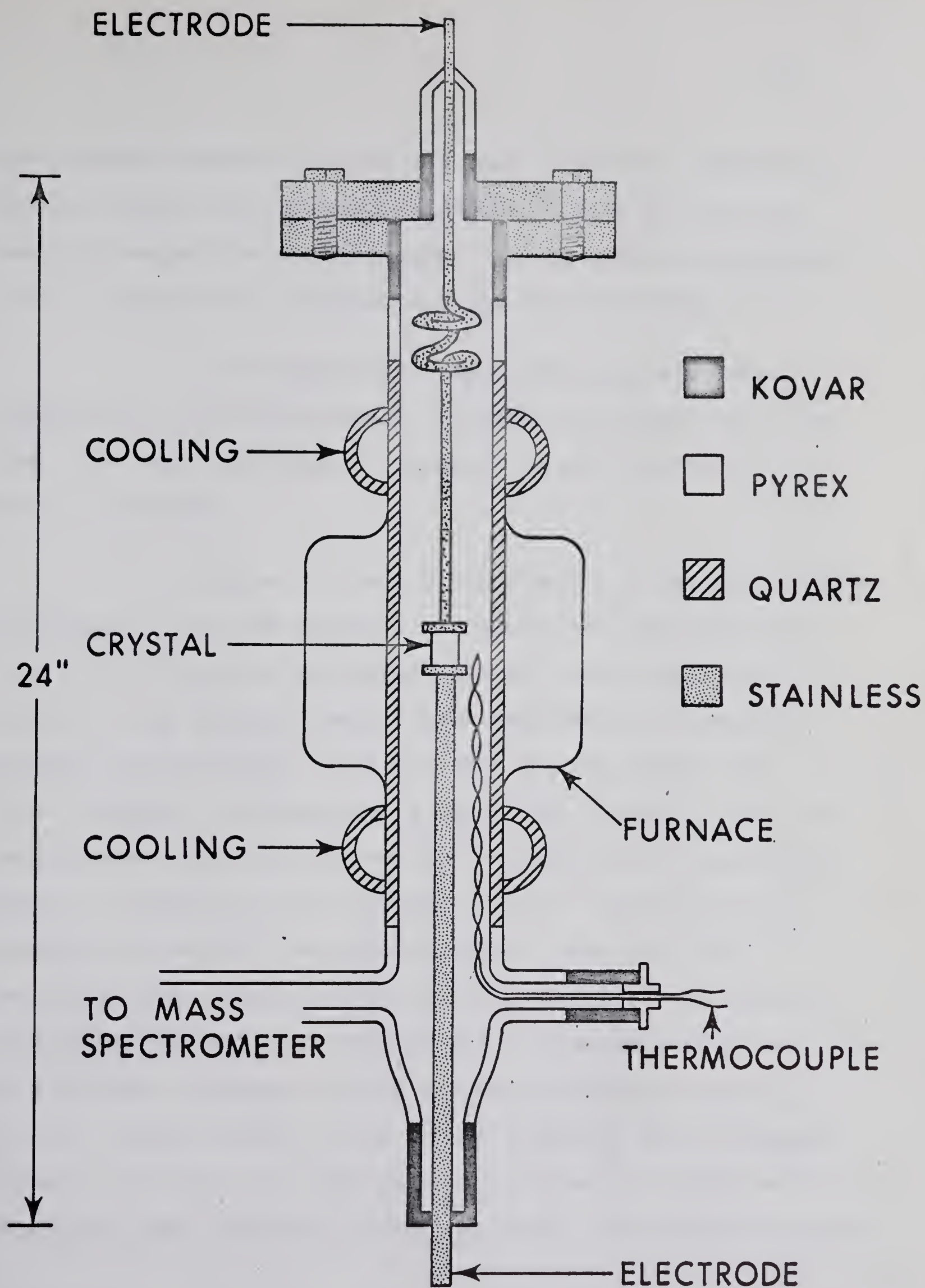


Figure I-1 Diffusion Conductivity Cell.

were mounted between the oven and quartz tube for temperature control, while the thermocouple mounted inside the cell is used for temperature measurements. An ice-water bath provided a 0° C. temperature reference for the cold junctions.

The temperature, argon flux, and electrical conductivity are simultaneously recorded as a function of the time. The mass spectrometer pressure at the ion pump can also be recorded.

Figure I-2 is a block diagram of the experimental arrangement. The gas from the diffusion cell goes directly into a 6-inch radius, 60 degree magnetic sector mass spectrometer. A RMI British Physical Labs megohmmeter is used to measure the resistance. The recorder cycles through the three channels corresponding to argon flux, conductivity, and temperature. All three curves are recorded on the same chart paper. A system is also available whereby the data can be directly punched on IBM cards concurrent with its visual recording, and analysed on an IBM 7040 computer. Preliminary tests with the IBM punch encountered considerable difficulty due to a 500 cps. component in the vibrating reed electrometer (V.R.E.) output signal. This is the frequency of the dynamic capacitor in the V.R.E. and while this gives no trouble with relatively slow responding chart recorders, the digital equipment

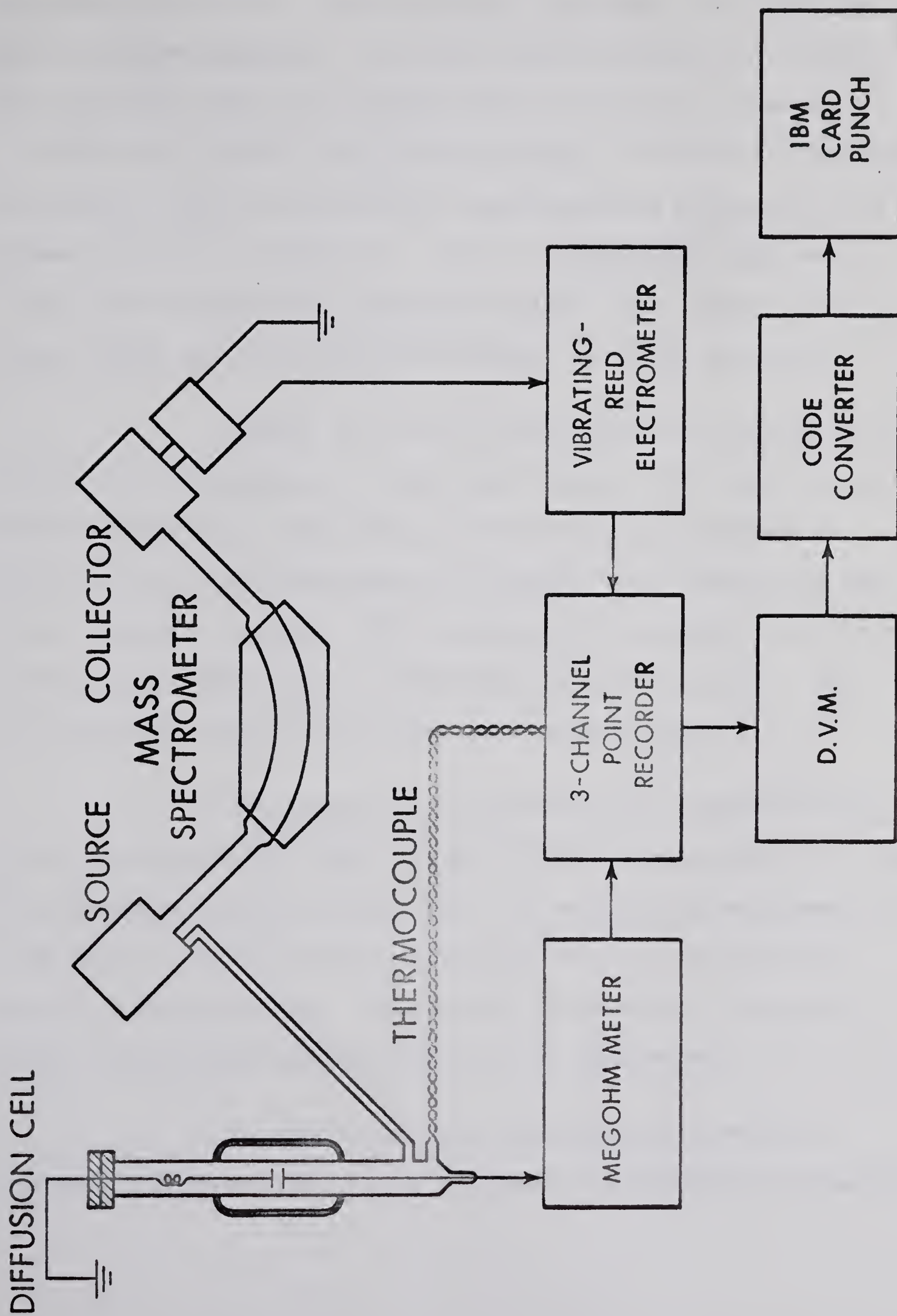


Figure I - 2 Block diagram of Experimental Equipment

was sensitive to it. The diffusion data were too scattered for suitable analysis. An ideal solution would be to equip the recorder with a re-transmitting slide wire connected to a stable D.C. source and use this signal to drive the digital voltmeter. Such a mechanical coupling would eliminate this undesirable A.C. component. Since the recorder used was on loan from the National Research Council, this modification wasn't made and the data were punched on cards manually.

Figure I-3 is an illustration of the manner in which the data appear on the chart paper. The three curves show temperature, argon flux, and electrical conduction. Note that as the temperature increases, both conduction and flux increase rapidly. (The conductivity usually stabilizes much more quickly than is indicated in this diagram. This is a special effect which will be discussed later.)

The argon flux increases with temperature but also decreases with time. It is for this reason that it rises to a maximum and then drops off. It supposedly decreases in time with a characteristic curvature which is dictated by the diffusion process. This is the "flux-time" curve for which theoretical expressions will be considered.

In order that the experimental curves be correctly interpreted, it is necessary to discuss the response

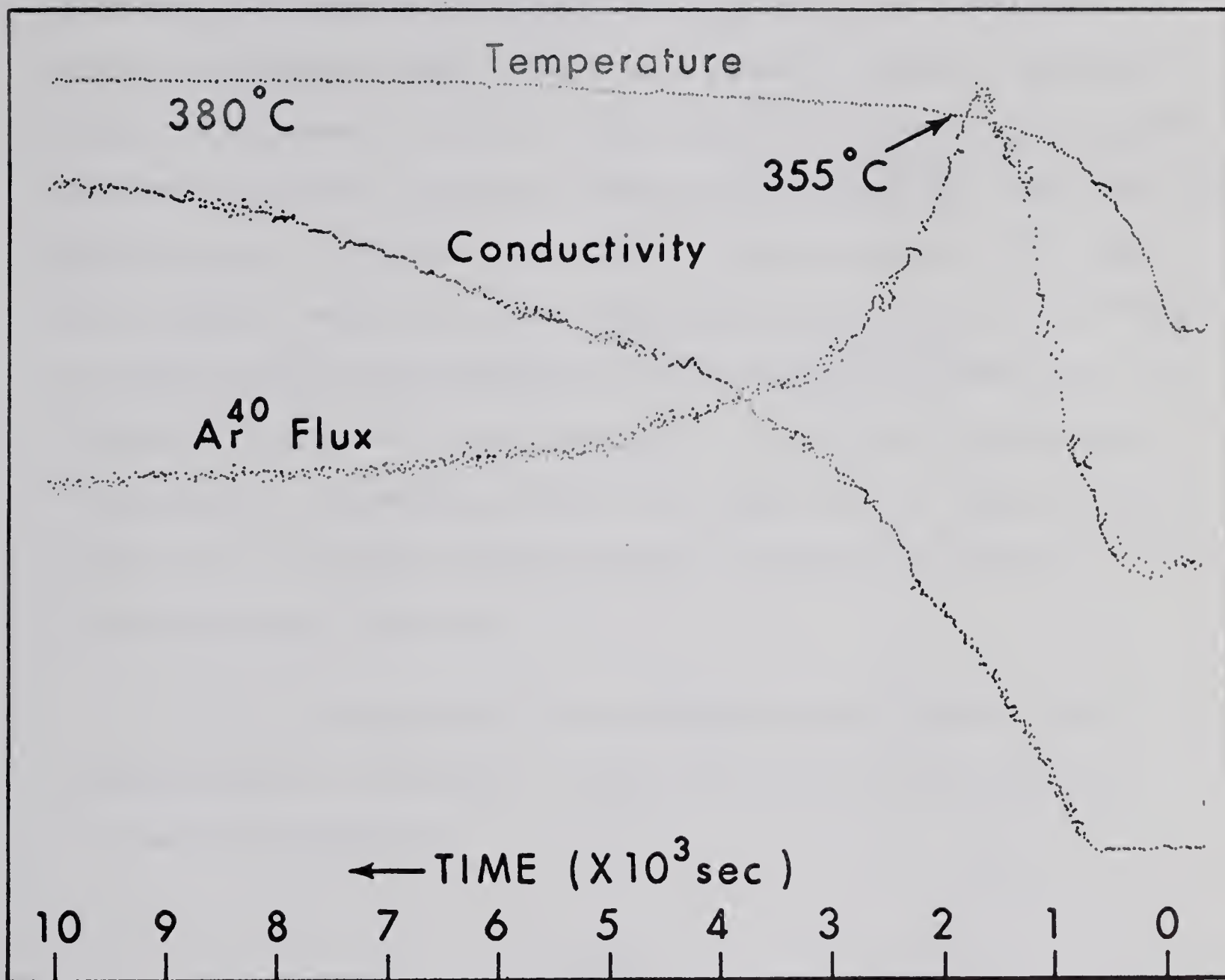


Figure 1-3 Illustration of Recorder Chart

of the mass spectrometer as a function of atomic flux in the ionization region. The gas is brought up to the ionization region from the diffusion cell by viscous flow due to a pressure differential between the diffusion cell and the mass spectrometer head. This is a natural pressure differential (as opposed to forced flow) caused by pumping the sampled gas away from the ionization area with a model 911-0012 VAC-ION getter pump. In order that the ion beam current of the mass spectrometer continues as a consistent indication of the flux of gas through the ionization box, the pumping speed must be constant throughout the experiment. According to the specifications of the manufacturer, the pump used in these experiments has a constant pumping speed to within 3% for the pressure range involved.

Figure I-4 is a diagram of the vacuum input system used for handling the gas prior to introducing it to the mass spectrometer.

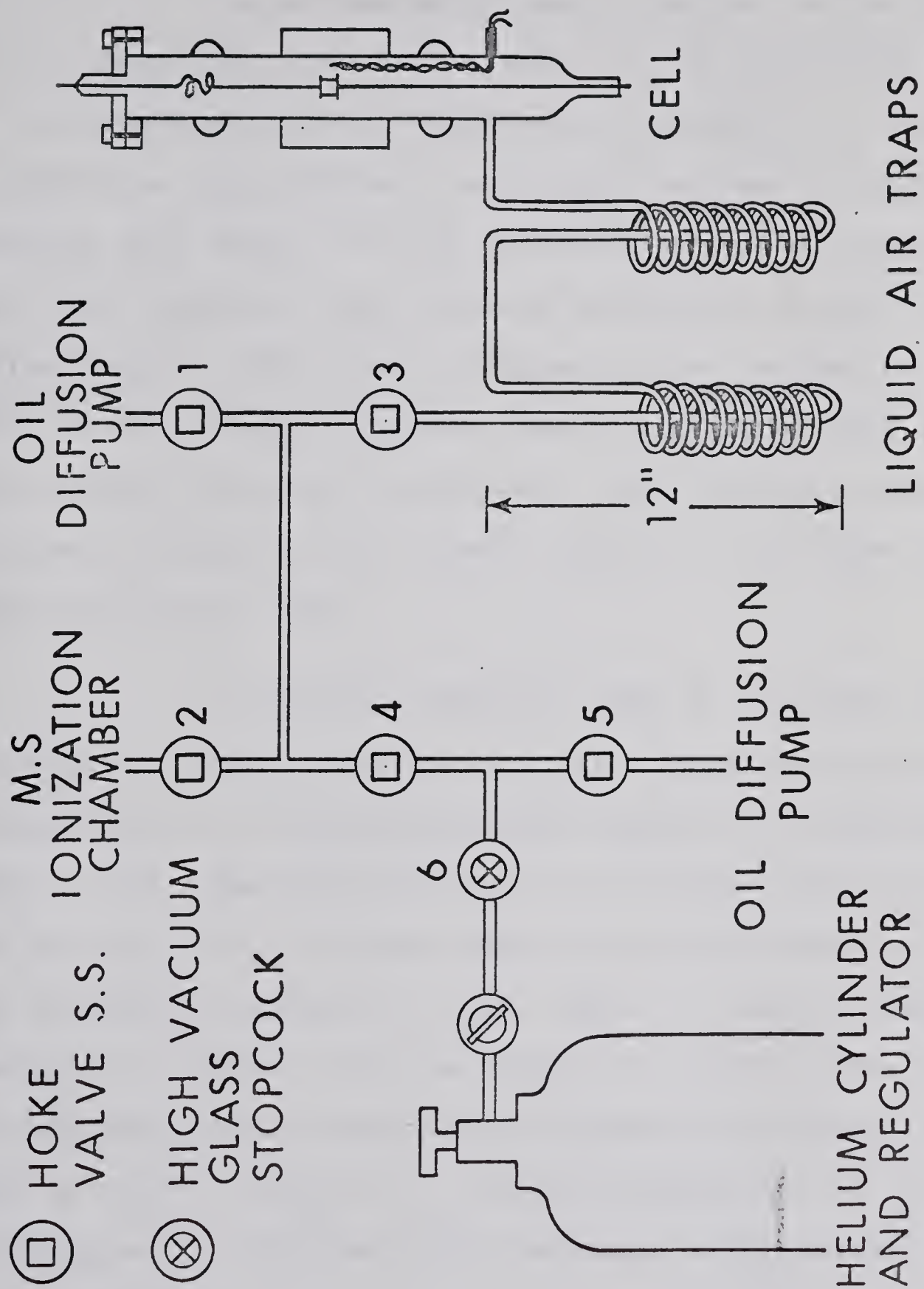


Figure I-4. Diagram of Vacuum Input System.

(B) MASS SPECTROMETER RESPONSE

A problem which must be solved before analysis of the flux-time curve can be made, is the functional form of the mass spectrometer response with pressure. Invariably, all previous experimenters have simply assumed a linear response when using the mass spectrometer for diffusion studies. They have considered the ion beam current to be directly proportional to the number of atoms in the ionization chamber. This is not strictly correct; however, it is a valid assumption for certain prescribed conditions. The following argument is taken from Burhop and Massey (1952) to illustrate the point we wish to make.

Consider a parallel beam of electrons of homogeneous velocity passing through a hypothetical gas consisting of N solid spherical atoms/cc. of cross-sectional area $Q \text{ cm}^2$. The probability of an electron being lost from the beam due to a collision with a gas atom after the electron has traveled a distance δx is $NQ\delta x$. If such an impact removes an electron from the beam, the change in the beam current due to its travelling a distance δx from a point P will be $\delta I = -NQI_p \delta x$. I_p is the current at P . If P is a distance x from the beam's starting point, the current will be given by

$$I_p = I_o \exp (-NQx) \quad I-1$$

The current of electrons lost from the beam, due to impact with gas atoms, is $I_o - I_p$. If we choose Q as the ionization cross-section, then $I_o - I_p$ will be the number of ions formed due to collisions of electrons with gas atoms.

Let p be the probability that an ion formed in the ionization region will reach the detector. Then the detected ion beam will be $I_i = p(I_o - I_p)$, or $I_i = pI_o(1 - \exp(-QNx))$. A plot of mass spectrometer ion beam current versus number of particles in the ionization chamber is given in figure I-5.

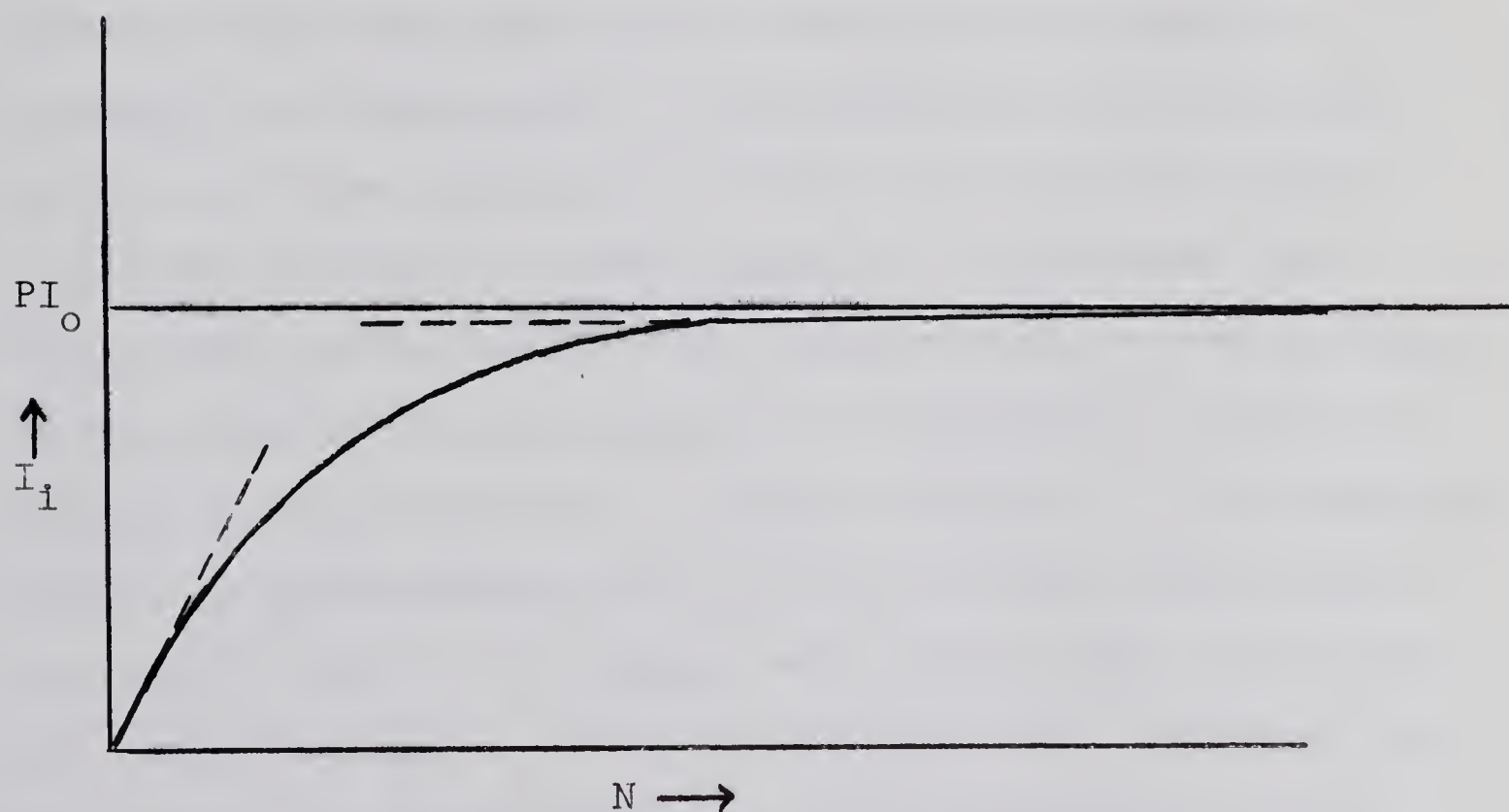


Figure I - 5

The response equation is $I_i = pI_o(1 - e^{-QNx})$ I-2

For extremely large N , $I_i \rightarrow pI_o$.

For extremely small N , $I_i \rightarrow pI_o QNx$.

It is seen that the ion beam current can be considered a linear function of the ionization chamber pressure in the asymptotic regions of the curve.

In intermediate pressure ranges, there will be pronounced curvature to the I_1 vs. N curve. This will have to be taken into consideration in any mass spectrometric experiment where there is variable pressure in the ionization chamber. Gas analysis measurements and isotope ratio experiments avoid this problem by using a large reservoir of sample gas and a molecular leak for introducing the gas to the ionization region. This keeps the input pressure constant and therefore the mass spectrometer response is a constant throughout the measurement. The experiments of this thesis cannot use these conditions, but must be done under viscous flow conditions with variable pressure on the input line. This forces one to consider the complete form of the ion beam current equation in the analysis of experimental results as opposed to simply assuming a linear response. If the pressures during the measurements are in the ultra high vacuum region (i.e. $<10^{-8}$ torr), the response will behave like the initial portion of the I_1 vs. N curve of figure I-5. This will be very close to a linear response. The experiments of this research have all been carried out in the ultra high vacuum region.

II. EXPERIMENTAL PROCEDURE

(A) Sample Preparation.

Crystal samples were prepared from a slab of material about 1/4 inch thick which was cut from the original specimen with a diamond saw. (One should note the crystallographic direction which will be perpendicular to the slab faces before proceeding further). The slab was then ground to approximately 0.04 cm. thickness using a sufficiently smooth lapidary wheel and grinding powder. The rough surfaces of this thin slab were etched with a dilute solution of hydrofluoric acid in order to remove the first few disordered atomic layers. Prior to loading into the diffusion cell, the sample was rinsed in acetone to remove any oil that may have been deposited on it during handling. The thin wafer was then placed between the electrode faces which are about one cm. square in area. Electrical contact was made by lightly pressing the electrode faces against the wafer. The spring was incorporated into the upper electrode to relieve the pressure on the sample during thermal expansion of the electrodes.

(B) Preparation and Loading of Conductivity-Diffusion Cell.

A standardized procedure was developed for preparing the diffusion cell in order to have the same initial conditions in the cell at the beginning of each run. This

involved a purging of the system with helium, at a temperature which was much higher than that used during the measurements. This was found to be necessary in order to reduce the mass 40 background contribution to a point where it did not significantly compete with the flux of gas coming from the crystal. The purging presumably forced helium into the walls of the diffusion cell displacing any atmospheric argon which may have been absorbed. This was found to completely eliminate background signal at low temperatures and sufficiently reduce it at high temperatures so that reproducible calibrations and corrections were possible.

The following outline refers to figure I-4 and gives a step-by-step listing of the exact procedure followed:

1. Valves 1, 2, 3, 4, and 5 are torqued to 30 inch-pounds.

High vacuum stopcock 6 is closed.

2. The crystal sample used in the previous run is removed from the diffusion cell.
3. The bolted flange is made vacuum tight with a new aluminum gasket by torquing the head bolts in a clockwise pattern using 10 inch-pound increments until at least 80 inch-pounds are applied to every bolt. (This is usually increased to 85 or 90 inch-pounds after preliminary pumping).
4. Valves 3 and 1 are opened and the system pumped down to

approximately 10^{-6} torr.

5. Glass lines and trapping coils are flamed out. The oven on the diffusion cell is brought up to 900°C . and maintained at this temperature for at least $\frac{1}{2}$ hour to drive out residual mass 40 material from the cell.
6. Valve 1 and the regulator valve are closed and valves 5 and 6 opened to pump out purging lines.
7. Valves 5 and 6 are closed and the regulator valve on the helium cylinder is adjusted to give a pressure reading of about ten pounds per square inch.
8. Valves 3 and 4 are opened while making certain that all other valves are sealed. Valve 6 is then gradually opened and the helium allowed to flow into the evacuated system. The temperature of the oven on the diffusion cell is maintained at 900°C . or higher.
9. All valves are sealed and the oven is allowed to cool to room temperature while the system remains at a positive pressure of helium.
10. When the oven has reached room temperature the bolted flange is opened and a crystal placed between the electrodes in the diffusion cell. The flange is then fastened according to step 3.
11. Valves 1 and 3 are gradually opened and the system pumped to approximately 10^{-6} torr. The glass lines and trap coils are flamed out, and the oven set to 50°C .

in order to gently desorb surface gases which may have remained on the surfaces of the crystal as a consequence of handling procedure. Pumping is continued for at least 1 or 2 days with the dry ice trap on the oil diffusion pump filled.

12. Twelve inch deep liquid air dewars are then placed around the glass coils. These liquid air traps were necessary to trap out other gases (mostly hydrocarbons) coming from the crystal and thereby unnecessary excessive pressure within the mass spectrometer was avoided. It was found that very deep dewars were required in order that the signal output of the mass spectrometer did not fluctuate significantly with changes in the liquid air level.
13. If a pressure of 10^{-8} torr. within the mass spectrometer is reached, then measurements may be started. If the pressure is considerably larger than this, the signal from the gas diffusing from the crystal is not sufficiently above that of the background. (The mass spectrometer signal can be increased by a factor of 6 by partially closing the valve in the pumping line between the ion pump and the head end of the mass spectrometer. One must be very careful when doing this however, since if it is closed beyond a certain point the flow of gas through the

ionization chamber becomes sufficiently impeded that dynamic gas flow conditions cease. If this increase of sensitivity is desired, it is necessary to ensure that dynamic flow is maintained by testing the rate at which a sample of gas is pumped from the ionization area. This time should be small compared to characteristic times in the experiment.)

Background data were taken for all temperatures by the same procedure to be outlined for obtaining diffusion data except step 9 is eliminated. The background contributions are then subtracted from the diffusion data.

14. Temperature settings are incremented in 50°C . steps and the flux time curves recorded for each setting. It was found that the data were more reproducible if the liquid air traps were removed and the coils pumped out prior to incrementing the temperature to the next value. Valve 2 is closed and 1 opened for this pump-out. Generally this pump-out is allowed to take place overnight while the cell is maintained at the temperature setting of the previous run. The next day, valve 1 is

closed, the liquid air dewars replaced, valve 2 opened and the data taken for the next temperature setting. These data are taken from three to twenty hours at each temperature depending on the size of the signal relative to the background contribution. Reliable diffusion data can be obtained from 200°C. to 800°C.

III. THEORETICAL FLUX-TIME CURVES

The basic problem in this section is determining the characteristic way in which an initial distribution of impurity substance will move or redistribute itself in the host material. In the present case, the impurity material is argon and the host material microcline feldspar. The crystalline material is in the form of a thin slab whose length and width is infinite in comparison to its thickness. If the manner in which the impurity material redistributes itself is known, then it is possible to determine the flux of diffusing substance which leaves the surface of the crystal as a function of the time.

Solutions to the problem of determining the flux at the surfaces of a thin doubly infinite slab are readily available in texts on diffusion and heat conduction in solids. (Crank 1959; Carslaw and Jaeger, 1959). These solutions are based on Fick's law of diffusion. This is done by applying the continuity equation

$$\frac{dC}{dt} = - \nabla \cdot F = - \frac{dF}{dy} \quad \text{III-1}$$

to Fick's first law

$$F = -D \frac{dC}{dy} \quad \text{III-2}$$

which results in the diffusion equation or Fick's second law

$$\frac{dC}{dt} = -D \frac{d^2C}{dy^2} \quad \text{III-3}$$

Figure III-1 defines the coordinate system for the above equations. "C" is the concentration of diffusing substance, "D" the diffusion coefficient, "F" the flux of diffusing substance and "t" the time.

Equation III-3 may be solved by the method of separation of variables to give the concentration as a function of position and time. Applying equation III-2 to this result gives the flux as a function of time.

Carslaw and Jaeger (1959, Chap. III) consider solutions to equation III-3 for various initial distributions. We shall examine the two limiting cases of a uniform initial distribution and a sine distribution.

For the case where the initial distribution is uniformly constant, the concentration as a function of position and time is given as,

$$C = \frac{4 C_0}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin (2n+1)(\pi y/l) \exp [-(2n+1)^2 \pi^2 D t / l^2]$$

III-4

applying equation III-2 gives the flux at the surface ($x=0, \ell$) as

$$F = \frac{8 DC_0}{\ell} \sum_{n=0}^{\infty} e^{-(2n+1)^2 \pi^2 Dt / \ell^2} \quad \text{III-5}$$

For small values of Dt , a more useful form of the flux time equation is given by Carslaw and Jaeger (1959) as

$$F = 2 DC_0 / (\pi Dt)^{\frac{1}{2}} \left\{ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2 \ell^2 / 4Dt) \right\} \quad \text{III-6}$$

The mathematical procedure for arriving at III-6 from III-5 is given in Titchmarsh (1937, pp. 60-65).

For the case of a sine distribution

$$C = C_0 \sin(2\pi y/\ell) \exp(-\pi^2 Dt/\ell^2) \quad \text{III-7}$$

and the flux at the surface is

$$F = - \frac{4 DC_0 \pi}{\ell} \exp(-\pi^2 Dt/\ell^2) \quad \text{III-8}$$

Equations III-4 and III-7 represent limiting cases of the concentration distribution within a thin slab. If one starts with a uniform distribution, the higher harmonics of III-4 will disappear first and after a sufficient time has

passed (depending on D and ℓ), the concentration will become a sine distribution. Equation III-7 shows that when a sine distribution has been established, it remains so and decreases in amplitude as a negative exponential of the time. This could be a very helpful result when applied to the interpretation of flux time data. Further discussion of the characteristic way in which the concentration changes shape may be found in Carslaw and Jaeger (1959, p. 99).

Equation III-6 may be used to determine values of D from flux time data if the initial distribution is uniform. If Dt is small enough a plot of F versus $1/t^{1/2}$ will be linear and its slope is given by $D^2 C_0 / \pi$. If the flux time data are taken with a mass spectrometer the sensitivity factor Ω will also appear in this slope. If m is the slope then $D = (\frac{m\pi}{\Omega C_0})^2$. Thus, in order to determine the diffusion coefficient it is necessary to know both Ω and C_0 . On the other hand, equation III-8 does not require a knowledge of these quantities. In this case, the initial distribution must be of the sine form and a plot of $\ln F$ versus t will give a slope whose only parameters are D and ℓ , the sample thickness. This allows for an absolute determination of the diffusion coefficient without recourse to concentrations or mass spectrometer sensitivity. Therefore, equation III-8 is in an ideal functional form as far as experiments of flux

time analysis with a mass spectrometer are concerned. Equation III-6 is extremely useful but not as accurate. For this reason, a method of developing flux time equations using a Green's function technique was investigated. This method, like the one previously described, allows for the use of various initial distributions. In the present work only a single distribution of the form $\sin y$ was tested.

The Green's function technique for solving diffusion and heat conduction problems is outlined in several texts (Morse and Feshbach, 1953; Carslaw and Jaeger, 1959). References to the original papers are given in Carslaw and Jaeger (1959). The use of the Green's function in solving the diffusion equation shall be presented here in outline form.

The Green's function is defined as the concentration at (x,y,z) at time τ due to an instantaneous point source of strength unity generated at the point $P(x_0,y_0,z_0)$ at time τ_0 , the solid being initially at zero concentration, and the surface being kept at zero concentration.

Let $G(\vec{r}, \tau | \vec{r}_0, \tau_0)$ be the Green's function which gives the concentration at point P with position vector $\vec{r}$ due to a unit source at P_0 with position vector $\vec{r}_0$. The concentration as a function of position and time due to an initial volume $f(r_0)$ distribution will be

$$c(\vec{r}, \tau) = \iiint G(\vec{r}, \tau | \vec{r}_0, \tau_0) f(\vec{r}_0) dx dy dz \quad \text{III-9}$$

All volume sources and surface distributions are considered zero.

The physical problem which must be handled mathematically is illustrated in figure III-1.

There exists a thin slab whose length and width shall be considered infinite, i.e., $\ell \ll \text{length or width}$. The diffusing gas is contained within the material and has some appropriate initial distribution. An equation is required which will predict the flux of gas coming from the surface of the crystal as a function of the time.

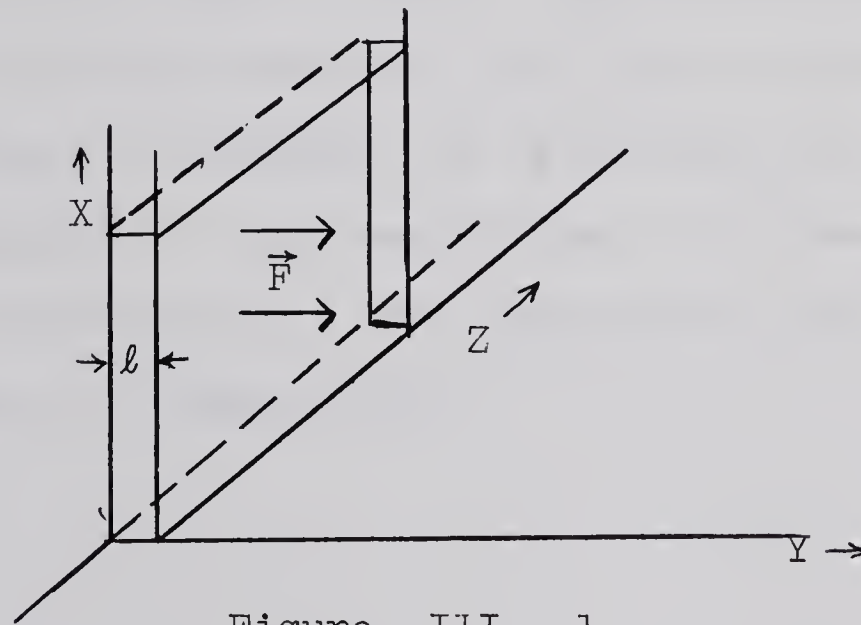


Figure III - 1

The Green's functions for diffusion in the infinite domain are given in Morse and Feshbach [1953]. A simplified discussion is given by Carslaw and Jaeger [1959].

The expressions for one, two and three dimensions are given below.

$$1 \text{ dimension } G(\vec{r}, \tau \mid \vec{r}_0, \tau_0) = A_1 \frac{e^{-a^2 R^2 / 4\tau}}{\sqrt{\tau}}$$

$$2 \text{ dimensions } G(\vec{r}, \tau \mid \vec{r}_0, \tau_0) = A_2 \frac{e^{-a^2 R^2 / 4\tau}}{\tau}$$

III-10

$$3 \text{ dimensions } G(\vec{r}, \tau \mid \vec{r}_0, \tau_0) = A_3 \frac{e^{-a^2 R^2 / 4\tau}}{\tau^{3/2}}$$

These are the Green's functions for the infinite domain. Since the present problem deals with a finite media, it is necessary to construct a Green's function which fits the associated boundary conditions. This can be done by a standard approach known as the method of images. [Morse & Feshbach, 1953, P. 812]. This is analogous to the image method of electrostatics. If a zero concentration boundary surface is required, it is obtained in a way which is analogous to the construction of a zero potential surface in electrostatics. The geometry of this method is illustrated in figure III-2.

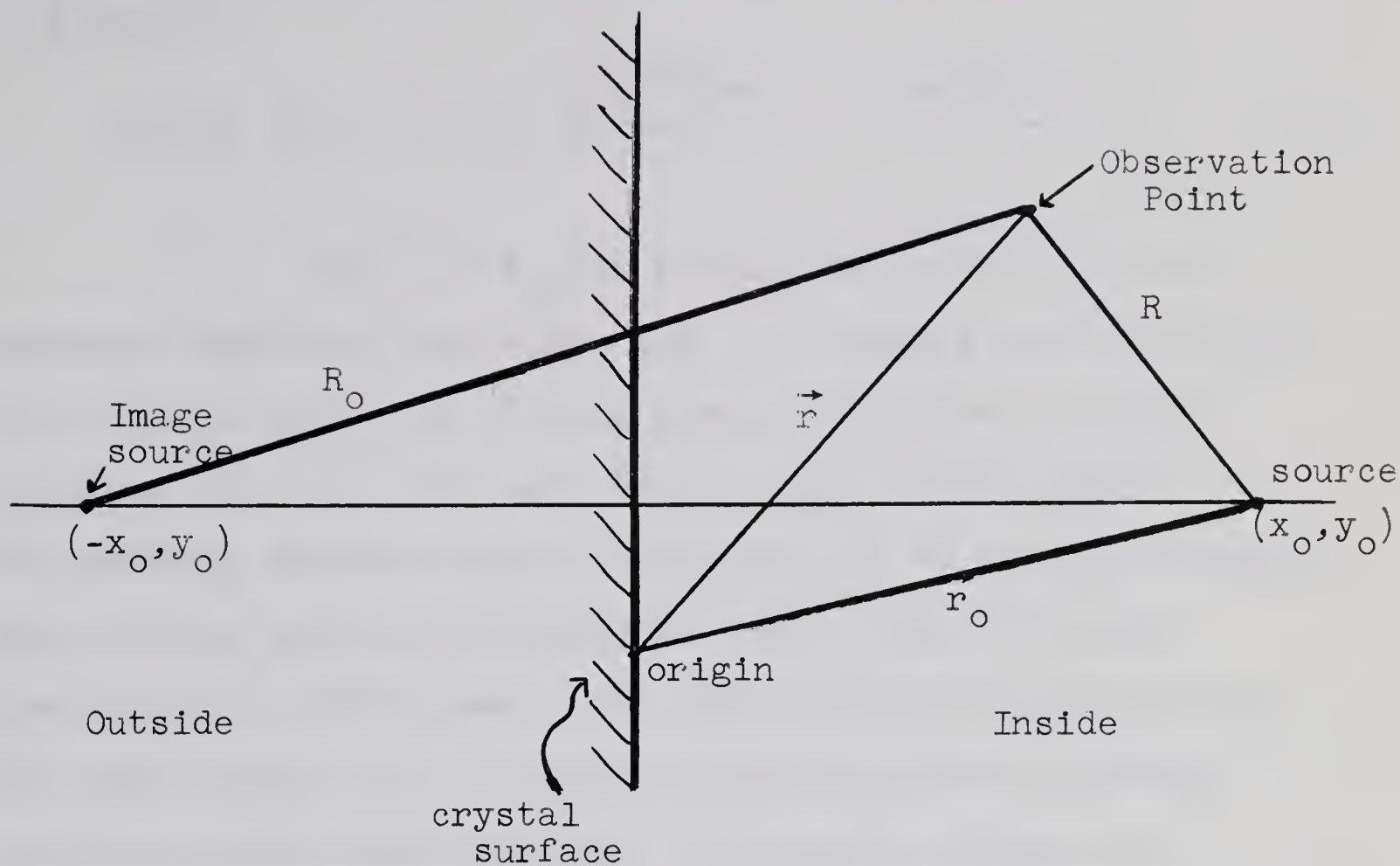


Figure III-2

A source of concentration of diffusing substance is placed inside the crystal at point x_o, y_o . A sink is placed at a corresponding distance outside the crystal face. (The sink may be thought of as a region depleted in concentration with respect to the overall background.)

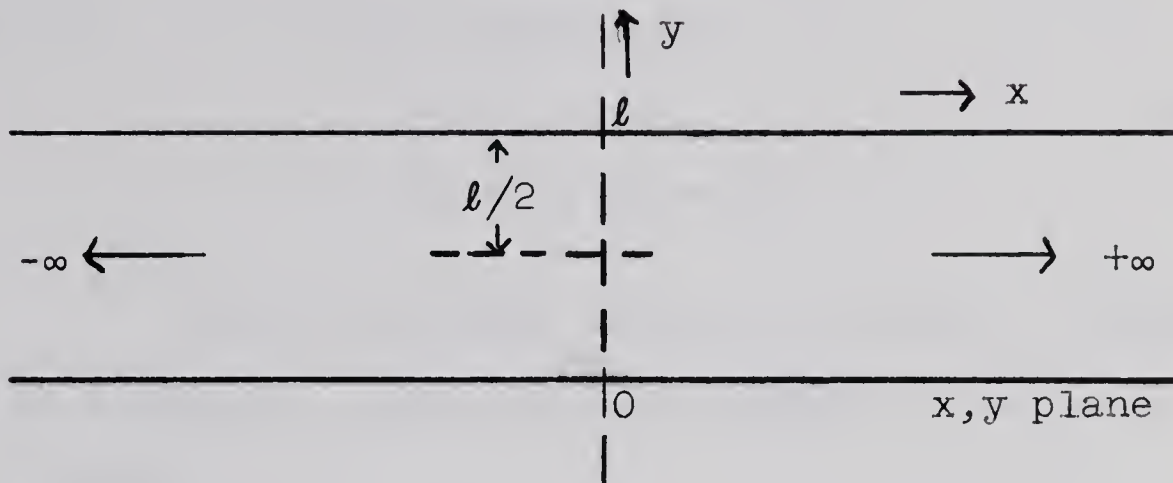
The total Green's function is then the combination of the real source and the vacancy source. These

combine to give a zero concentration plane at the crystal surface. The total Green's function for the region > 0 is given as:

$$G(\vec{r}, \tau | \vec{r}_0, \tau_0) = A_2 \left[\frac{e^{-a^2 R^2 / 4\tau}}{\tau} - \frac{e^{-a^2 R_0^2 / 4\tau}}{\tau} \right] \quad \text{III-11}$$

When $R = R_0$, the G function is zero, and the boundary conditions are satisfied. In working out the details for the thin slab, one becomes involved with two boundary surfaces. (i.e. one for each face of the crystal wafer.) The boundary surfaces may be accounted for by multiple images; however this leads to an infinite series with the usual limitations of usefulness. The infinite series results from the image source for one surface unbalancing the boundary condition of the other surface. Successive attempts to counter balance these interactions results in an infinite series of correction terms. (For a discussion of this problem see Morse & Feshbach [1953, P. 814].) A simple way to eliminate this problem is to mathematically transform the doubly bounded region to a singly bounded region. The methods of conformal mapping supply the necessary procedures for doing this. The following discussion outlines the steps involved, and the details are given in appendix I.

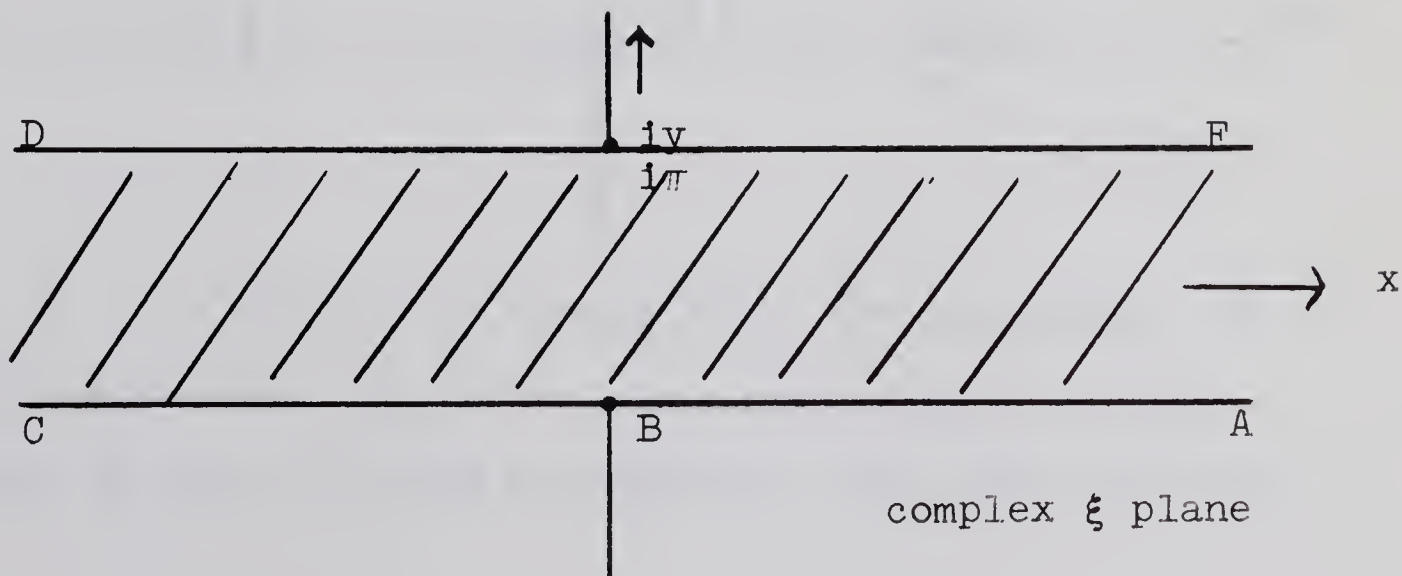
A cross-sectional view of the real crystal slab would appear as follows



If the geometry of the crystal slab was set up in the complex plane, it could be represented as follows:

$$i\xi = x + iy$$

The scale is arranged such that $l = \pi$



The following conformal mapping of the boundaries may be performed: [Churchill, 1960]. (Fig. 6 Appendix 2).

$$w = e^z$$

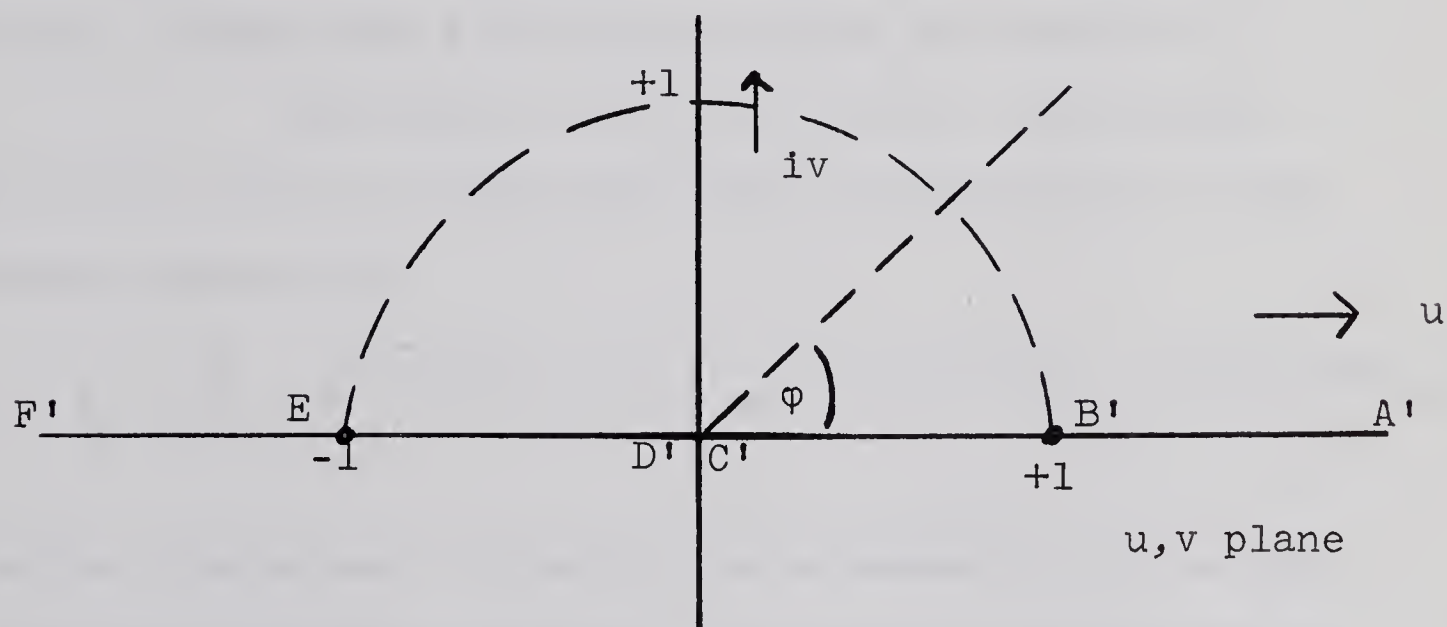
$$x + iy = F(u + iv)$$

$$w = u + iv$$

III-12

$$z = x + iy = i\xi$$

This transforms lines of constant x values to arcs of constant ρ , and lines of constant y value to rays of constant φ .



A point Z is any point in the x, y plane. No restrictions shall be placed on Z except that the boundary conditions in the x, y plane be defined. This will allow for

the use of any arbitrary initial distribution. The form of the initial distribution will be encountered in the x,y plane which is the real cross-section of the crystal. The Green's function on the other hand must be defined originally in the u,v plane. This is an important distinction since it requires a two dimensional cartesian coordinate Green's function in the u,v plane to describe a one dimensional diffusion in the x,y plane. This is because the single dimension of y has been transformed to a two dimensional arc in the u,v plane. The distribution used in the real crystal will have to be transformed to the appropriate distribution in the u,v plane. This is straight forward and a discussion given in Appendix I.

The Green's function for two dimensional diffusion in the u,v plane with zero concentration at the boundary surface is

$$G_w = \frac{A_2}{\tau} e^{-a^2/4\tau(u-u_0)^2} \left[e^{-(v-v_0)^2 a^2/4\tau} - e^{-a^2/4\tau(v+v_0)^2} \right]$$

This two dimensional G function is necessary since we are applying G functions derived in cartesian co-ordinates to a situation where diffusion is constrained to an arc of radius ρ in the u,v plane. If these G functions had been originally derived in polar co-ordinates, then the one di-

mensional function would be appropriate to describe diffusion constrained to an arc of radius ρ . This one dimension would be the ϕ co-ordinate.

The effect of an initial distribution on the concentration at a latter time is given by

$$\psi(\vec{r}, \tau) = \lambda \int [\psi_0 G] dv \quad \text{III-13}$$

τ is time, ψ_0 is the initial distribution. The integration is carried out over the coordinates of the initial distribution.

Therefore the concentration of diffusing substance in the u, v plane will be given as

$$\psi_w = A \int \psi_{ow} G_w dA \quad \text{III-14}$$

ψ_{ow} is the distribution in the u, v plane.

G_w is the Green's function in the u, v plane.

Before evaluating these integrals, it is more convenient to formulate the G function in polar co-ordinates.

$$G_w = \frac{A}{\tau} \left[e^{-a^2 R_1^2 / 4\tau} - e^{-a^2 R_2^2 / 4\tau} \right] \quad u + iv = \rho e^{i\phi}$$

$$u = \rho \cos \phi \quad v = \rho \sin \phi$$

$$u_0 = \rho_0 \cos \phi_0 \quad v_0 = \rho_0 \sin \phi_0 \quad \text{III-15}$$

$$R_1^2 = \rho^2 + \rho_0^2 - 2\rho\rho_0 \cos \phi \cos \phi_0 - 2\rho\rho_0 \sin \phi \sin \phi_0$$

$$R_2^2 = \rho^2 + \rho_0^2 - 2\rho\rho_0 \cos \phi \cos \phi_0 + 2\rho\rho_0 \sin \phi \sin \phi_0$$

(notice that at $\varphi = 0, \pi$ the function will be zero and therefore still satisfies the boundary conditions).

G_w becomes:

$$G_w = A/\tau \{ \exp [-a^2(\rho^2 + \rho_o^2)/4\tau] \exp [2a^2\rho\rho_o \cos \varphi \cos \varphi_o/4\tau] \times \\ \times \sinh [2a^2\rho\rho_o \sin \varphi \sin \varphi_o/\tau] \} \quad \text{III-16}$$

Under the transformation, ρ is a constant and dA goes over to $d\varphi$.

$$\psi = A/\tau \{ \exp [-a^2(\rho^2 + \rho_o^2)/4\tau] \int_0^\pi \psi_{ow} \exp [2a^2\rho\rho_o \cos \varphi \cos \varphi_o/4\tau] \times \\ \times \sinh [2a^2\rho\rho_o \sin \varphi \sin \varphi_o/4\tau] d\varphi_o \}. \quad \text{III-17}$$

Let $2a^2/4\tau = \alpha$, $\cos \varphi = \beta$, $\sin \varphi = \gamma$ and integrate over the source co-ordinates

$$\alpha\beta\rho\rho_o = K$$

$$\alpha\gamma\rho\rho_o = \delta$$

$$\psi = A/\tau \{ \exp [-\alpha(\rho^2 + \rho_o^2)/2] \int_0^\pi \psi_{ow} \exp [K \cos \varphi_o] \sinh [\delta \sin \varphi_o] d\varphi_o \}$$

III-18

where ψ_{ow} is the initial distribution.

Equation III-18 may be written as

$$\psi = \frac{A}{\tau} e^{-\alpha(\rho^2 + \rho_o^2)/2} I$$

Thus the problem of calculating the concentration as a function of position and time is reduced to an evaluation of the following integral.

$$I = \int_0^\pi \psi_o(\varphi_o) e^{K \cos \varphi_o} \sinh(\delta \sin \varphi_o) d\varphi_o \quad \text{III-19}$$

This is a definite integral involving functions of sine and cosine. The method of contour integration in the complex plane can be used to evaluate III-19.

The contribution, which this integral makes to the flux time equation, is determined in Appendix II. This is written as,

$$I = 2\pi \left\{ 1.51 + (.5) \cosh (\sqrt{.7} K) \right\} + w' \quad \text{III-20}$$

Incorporation of this result into Eq. III-18 and the calculation of the flux-time equation from it are given in Appendix III. This results in an expression for the flux at the surface of the crystal which is given by:-

$$|F| = C_0 \left(\frac{2\ell^{3/2}}{4\pi^{3/2} D^{1/2}} \right)^2 \frac{e^{-\frac{\ell^2}{2\pi^2 D \tau}}}{\tau^2} \left\{ 1.51 + (.5) \right. \\ \left. \cosh\left(\frac{.42\ell^2}{\pi^2 D \tau}\right) \right\} \quad \text{III-21}$$

$|F|$ is the flux from the surfaces of the crystals

ℓ = thickness of crystal slab

D = diffusion coefficient

τ = time

If $D \geq 10^{-8}$ cm²/sec., this expression may be reduced to

$$|F| = (2.01) \left(\frac{\ell}{2\pi} \right)^2 \frac{C_0 \ell}{\pi D} \frac{e^{-\frac{\ell^2}{2\pi^2 D \tau}}}{\tau^2} \quad \text{III-22}$$

If $D < 10^{-8}$ cm²/sec.,

$$|F| \approx \frac{1.43 C_0}{(.16)} \left(\frac{\ell^{3/2}}{2\pi^{3/2}} \right) \frac{e^{-\frac{(.16)\ell^2}{2\pi^2 D \tau}}}{D \tau^2}$$

Comparison of equation III-22 with III-8 shows that the diffusion coefficient given by each are in agreement within the present experimental error. There were no approximations required in arriving at equation III-8; however several assumptions and approximations were made in arriving at III-22. Despite this difference, equations III-22 and III-8 may be considered equivalent for the purposes of this present study.

IV. PRESENTATION AND ANALYSIS OF DATA

Figure IV-A shows a plot of $\ln V_{\max}$ versus reciprocal temperature. $V_{\max}$ is the maximum value of the mass spectrometer signal during any one diffusion anneal. This will occur at the very beginning of the flux time curve. $\ln V_{\max}$ is a smoothly varying function of the diffusion coefficient (see section VII) and any discontinuous change in the experimental curve will indicate a discontinuity in the diffusion coefficient. A major change in $\ln V_{\max}$ is seen to occur between 450°C and 500°C . This is supported by a change of activation energy in the Arrhenius plot of conductivity. A second break in these curves occurs between 600°C and 650°C . Amirkhanoff [1961] has observed an identical break of the Arrhenius plot for argon diffusion in feldspar at 650°C . The inset of Figure IV-A is a specific heat curve for feldspar as published by Amirkhanoff [1961]. He classifies it as a second order transition. However, the shape of the specific heat curve is not conclusive and differs from the expected behavior. It would be interesting to see data over a wider temperature range. Examination of the conductivity curves (Figures IV-5 to IV-7) in the neighborhood of the 450°C transition shows that a large density of point defects are being created at these temperatures. Analyses of the diffusion data will be complicated by these large defect concentrations and subsequent structural transitions in microcline. The

transitions are present in the data for electrical conductivity [Pronko 1962], specific heat [Amirkhanoff, 1961] and the argon diffusion results of the present work. Ham [1937], Ham and Rast [1938] and Coleman and Yeagley [1944] have shown that gas diffusion in solids will be very sensitive to structural transitions. The fact that the transitions at 450° C and 600° C manifest themselves in more than one physical phenomena is proof of their reality. However, the precise nature of these transitions is another problem. It will be shown later that they can be correlated with the phase diagram of Smith [1960] and that atomic disordering could be responsible for the transitions. For the moment it is only necessary to know that these effects are present and that allowance must be made for their possible influence on the flux-time curves and conductivity-time curves. Because of the magnitude of the first transition, the diffusion data will be analyzed in terms of its behavior above and below 500° C.

Errors

The probable error in the value of D as calculated from the equations of Section III is of the order of 6%. This will be caused by variations in the thickness (i.e. non parallel surfaces) of the slab and by the regression residual of the curve fit. However, the experimental reproducibility might vary from 30 to 50% and may be accounted for by the following additional sources of error:

- (1) The sample is not really an infinite slab as required by theory. The edge area of the slab is $\sim 2\%$ that of the two main parallel surfaces.
- (2) There will be slight deviations in diffusion direction when going from one sample to the next due to non-reproducible cutting. The error here is difficult to estimate but is thought to be less than 5%.
- (3) A significant error will be introduced in the determination of background signal. The background must be determined as a separate experiment and, in spite of the purging procedure, is not exactly reproducible each time the vacuum is broken. The error introduced by this will be small during the early part of the flux-time curve but will increase at longer times. In the first thirty minutes of the diffusion anneal this error will be less than 10%. At the beginning of the run it is approximately 0.1% and

may increase to $\sim 10\%$ after thirty minutes. In two hours this error could be as high as 30% and would increase correspondingly at larger times.

- (4) An additional complicating factor which makes reproducibility difficult is the possibility of dislocation diffusion. It is probable that at low temperatures ($T < 500^{\circ} \text{C}$) the gas release is dominated by diffusion along dislocations. Since the dislocation pattern and density may vary from one sample to the next, it would be difficult to obtain reproducible results from such a mechanism.
- (5) The final factor which makes reproducibility difficult in the present study is phase transformations. The 450°C transformation is observed to occur very slowly over a wide temperature range. A lesser transformation appears to exist near 300°C and another more significant one at 600°C . Diffusion anneals in the area of these temperatures will not be reproducible since the crystal will not be in thermodynamic equilibrium during the time when the gas release curve is being observed. Thermodynamic equilibrium is not accomplished until several hours after the crystal has been maintained at a given temperature in the neighborhood of the transition.

The minimum total error in the absolute value of the diffusion coefficient will be no less than 20% under any circumstances and may get as high as 50 to 100% where dislocation diffusion is being observed and/or in temperature regions of crystallographic instability.

Measurements of electrical conductivity have only been pursued in a qualitative way since no account of surface conductivity and electrode contact was made in the measurements. The relative changes in conductivity with temperature are significant, but absolute values for the conductivity cannot be quoted. For this reason, the conductivity data have been presented in terms of relative values or in arbitrary units.

(A) Data below 500° C.

Examination of the flux-time curves (Figures IV-1 to IV-7) reveals that the diffusion coefficient is greater than 10^{-8} cm²/sec. This is determined by comparing the normalized flux-time decay curve to the infinite series result of equation III-5. Similar experimental and theoretical decay curves are obtained when only the first few terms of the infinite series are used. This means equations III-8 and III-22 may be used to determine the value of D for temperatures below 500° C. Since a large diffusion coefficient is in effect at these low

temperatures, the equation utilizing a sine distribution should be appropriate for the analysis. The diffusion coefficients and activation energies as calculated by the above method are presented in Table I. Consideration of the fit of the experimental curves to the theoretical ones will be deferred until part C of this chapter.

(B) Data above 500° C (Figures IV-8 to IV-13)

All attempts to analyze the flux-time curves above 500° C using equations III-8 and III-22 fail. Comparison of the infinite series results of equation III-5 with the flux-time equations above 500° C indicates that the diffusion coefficient is much smaller than 10^{-8} cm²/sec. It appears that the transformation between 450° C and 500° C has resulted in a structural change within the crystal and an environmental change for the argon. This new environment is such that the diffusion coefficient for argon is much lower. It is also possible that a general redistribution of argon within the lattice has occurred.

Equation III-6 is in a form especially suited for small diffusion coefficients. If D is less than 10^{-8} cm²/sec the exponential terms become negligible and the flux simply drops off as $1/t^{\frac{1}{2}}$. This equation assumes that the initial

TEMP.	D #64	D #65	D #66	MEAN ACTIVATION ENERGY
200°C		$6.54 \times 10^{-8} \pm .37$	$1.96 \times 10^{-8} \pm .27$	(Thermal Diffusion Only)
250°C		$4.40 \times 10^{-8} \pm .53$	$2.20 \times 10^{-8} \pm .06$	
300°C	$8.5 \times 10^{-8} \pm .21$	$5.62 \times 10^{-8} \pm .30$	$2.37 \times 10^{-8} \pm .09$	
350°C	$1.1 \times 10^{-7} \pm .10$	$6.76 \times 10^{-8} \pm .54$	$2.33 \times 10^{-8} \pm .07$	
400°C	$3.3 \times 10^{-7} \pm .24$	$2.39 \times 10^{-7} \pm .17$	$3.20 \times 10^{-7} \pm .15$	
450°C		$9.27 \times 10^{-8} \pm .16$	$5.48 \times 10^{-8} \pm .24$	2.85 ± 0.7
500°C				
550°C	$\sim 3.2 \times 10^{-12}$	$\sim 9 \times 10^{-12}$		
600°C	$\sim 1.5 \times 10^{-11}$	$\sim 1.5 \times 10^{-11}$		35 ± 9
650°C	$\sim 2.8 \times 10^{-12}$	$\sim 3 \times 10^{-11}$		
700°C	$\sim 2 \times 10^{-12}$	$\sim 2.3 \times 10^{-12}$		26.4 ± 6
750°C		$\sim 3.4 \times 10^{-12}$		
800°C		$\sim 7.8 \times 10^{-12}$		

Table I Diffusion Coefficients (Cm^2/sec) and Activation Energies
(K Cal/Mole).

(D values above 500°C are only approximate)

distribution is uniform throughout the crystal. For a small diffusion coefficient, a uniform distribution would be retained for a long time if it were present initially. The uniform distribution may or may not be the case. The large diffusion coefficient at the lower temperatures should tend to promote a sine distribution. On the other hand, the transition may have permitted some redistribution of the argon so that it tended back towards a uniform distribution.

When the flux-time equation is in the form of III-6, it does not lend itself very well to the analysis of flux-time curves taken with a mass spectrometer. The reason lies in the fact that the mass spectrometer output is proportional to the flux, i.e. $V = \beta F$. The proportionality constant β is required if equation III-6 is used to analyze the flux-time curve. If the flux is given in terms of exponentials, it is usually possible to eliminate the need for β through the use of logarithms. At present, such an equation is not available for small diffusion coefficients and one is consequently forced into evaluating the sensitivity factor β . There are two ways to handle this situation. The first is to directly determine β by calibration of the mass spectrometer. This can be done by introducing a known flux of gas into the instrument. An alternative procedure is to simply compare values of βD to

values of the diffusion coefficients as determined by other techniques. In the present study the latter procedure was chosen. Values of activation energies for the diffusion process may be determined by making an Arrhenius plot of βD versus $1/T$. Such a plot is presented in Figure IV-14.

Comparison is made with a similar plot by Amirkhanoff [1961] who used an isotope dilution technique to determine the diffusion coefficients for temperatures above 500° C. Table I contains comparisons of the activation energies of the present study with those of Amirkhanoff [1961]. A mean value for the sensitivity factor may be determined in this way. The value of β is not an absolute characteristic of the instrument since it also involves the surface area of the sample being studied. However, it is a characteristic value for any one set of flux-time curves taken with a particular sample.

(C) Relative fit of the experimental and theoretical curves.

The degree of matching of experimental and theoretical curves is a test of the initial assumptions made in deriving the theoretical curve. The equations used so far in analyzing the diffusion data are ones which assume normal diffusion according to Fick's laws. They differ in the assumed initial distribution.

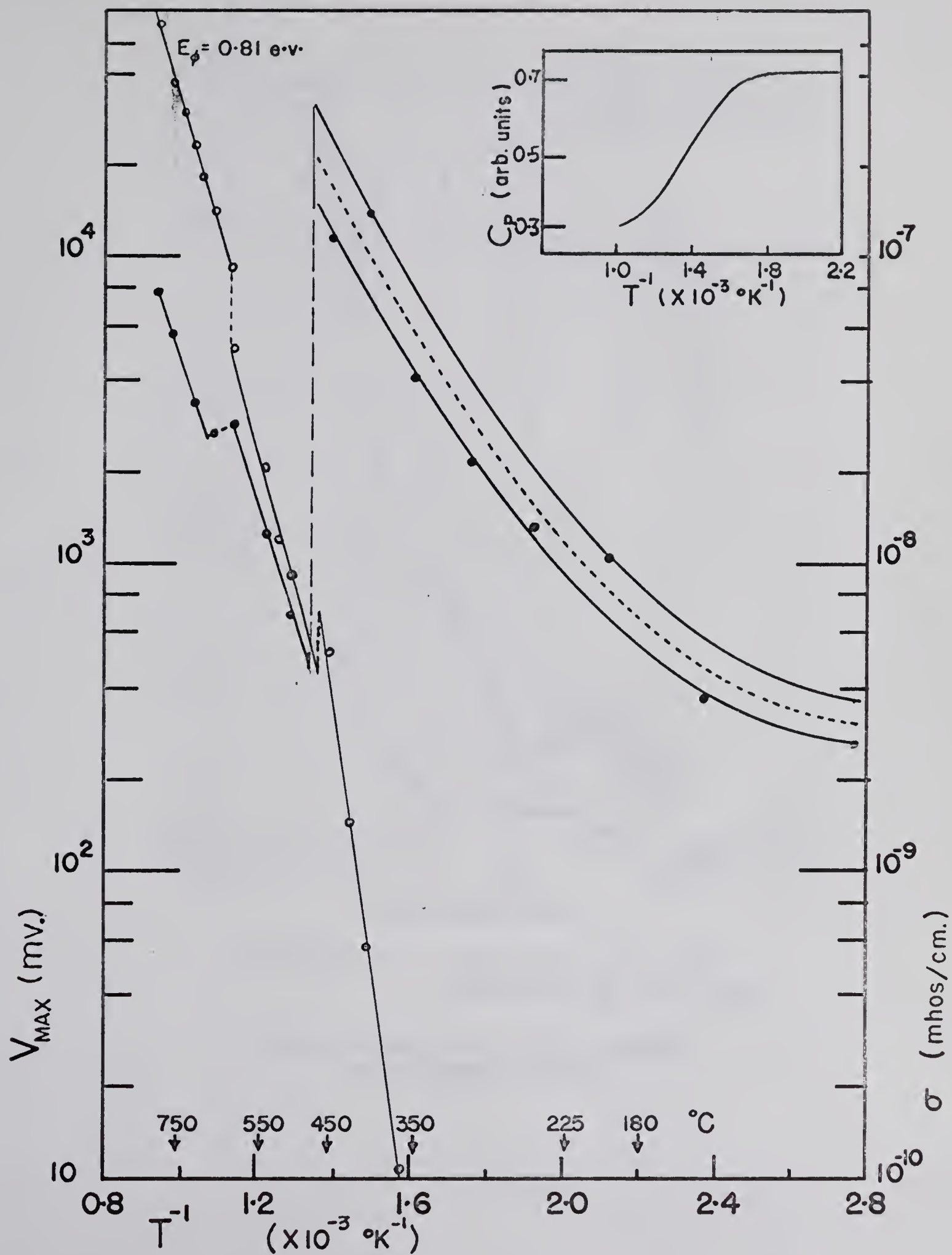


Figure IV-A. $\ln V_{\text{max}}$ vs. $1/T$; $\ln$ conductivity vs. $1/T$
 (from Pronko, 1962); Specific Heat vs. $1/T$
 (Amirkhanoff, 1961).

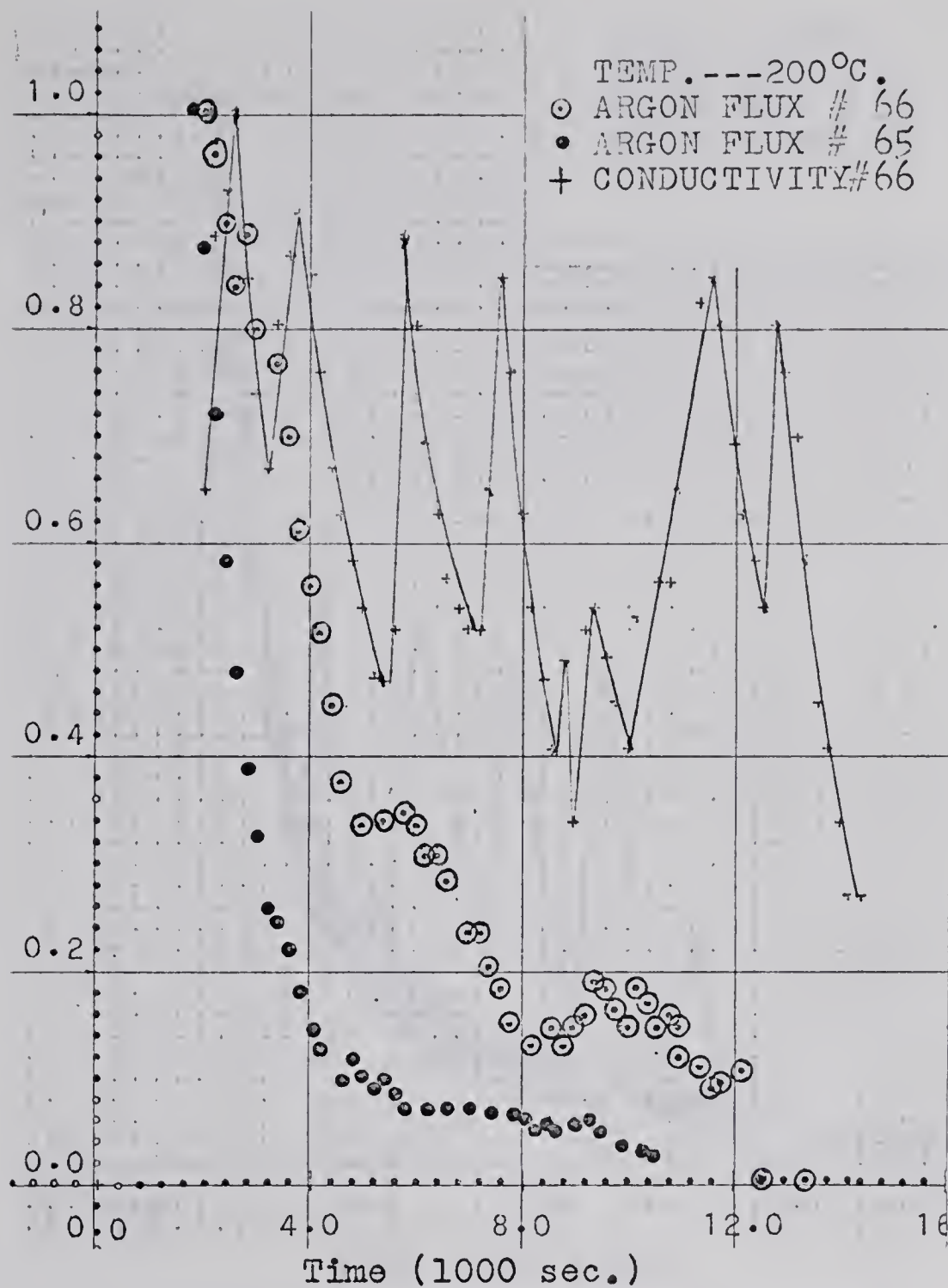


FIGURE IV-1 ARGON FLUX VS. TIME
CONDUCTIVITY VS. TIME

(Data normalized with respect
to maximum value)

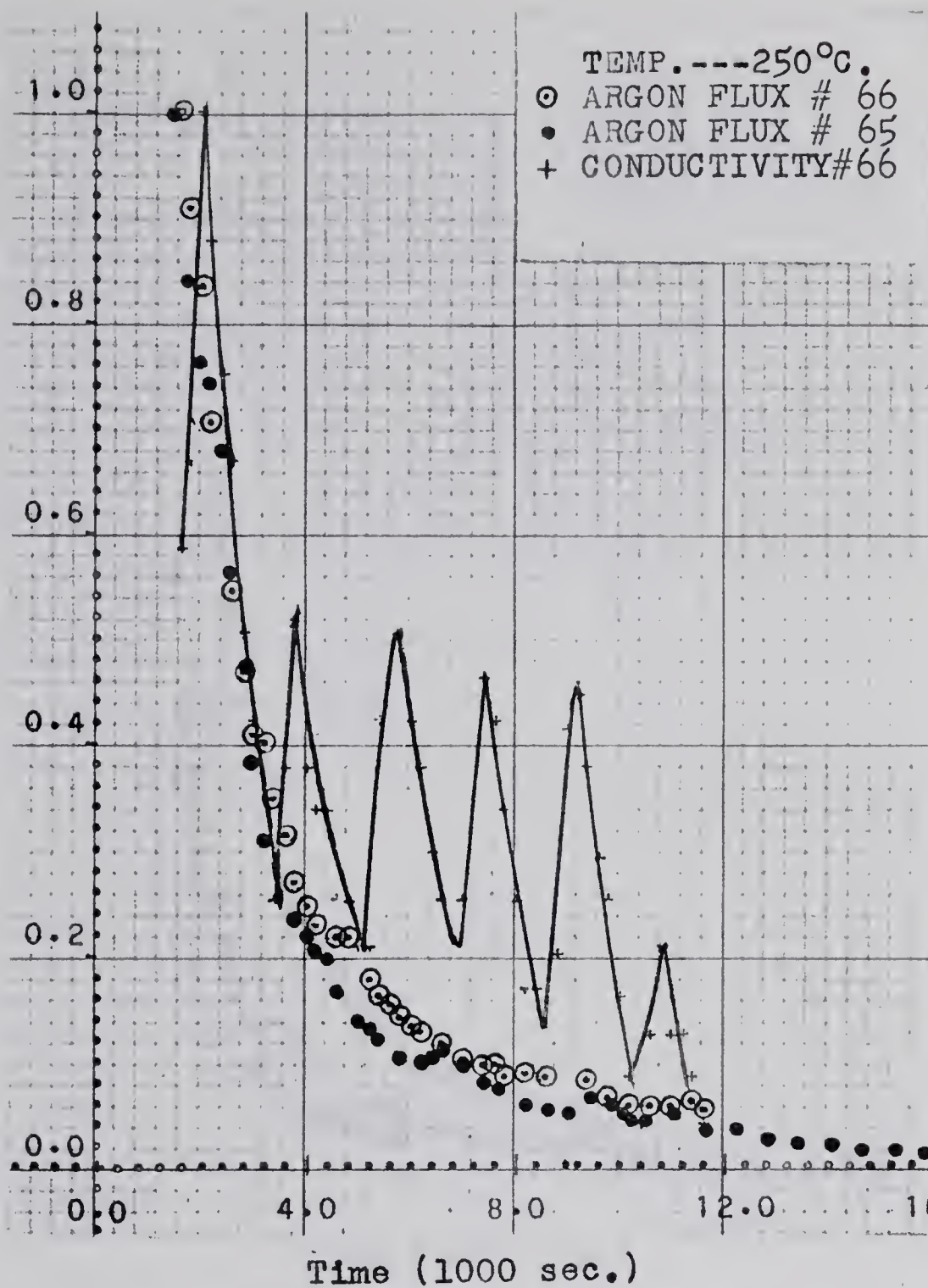


FIGURE IV-2 ARGON FLUX VS. TIME
 CONDUCTIVITY VS. TIME

(Data normalized with respect
 to maximum value)

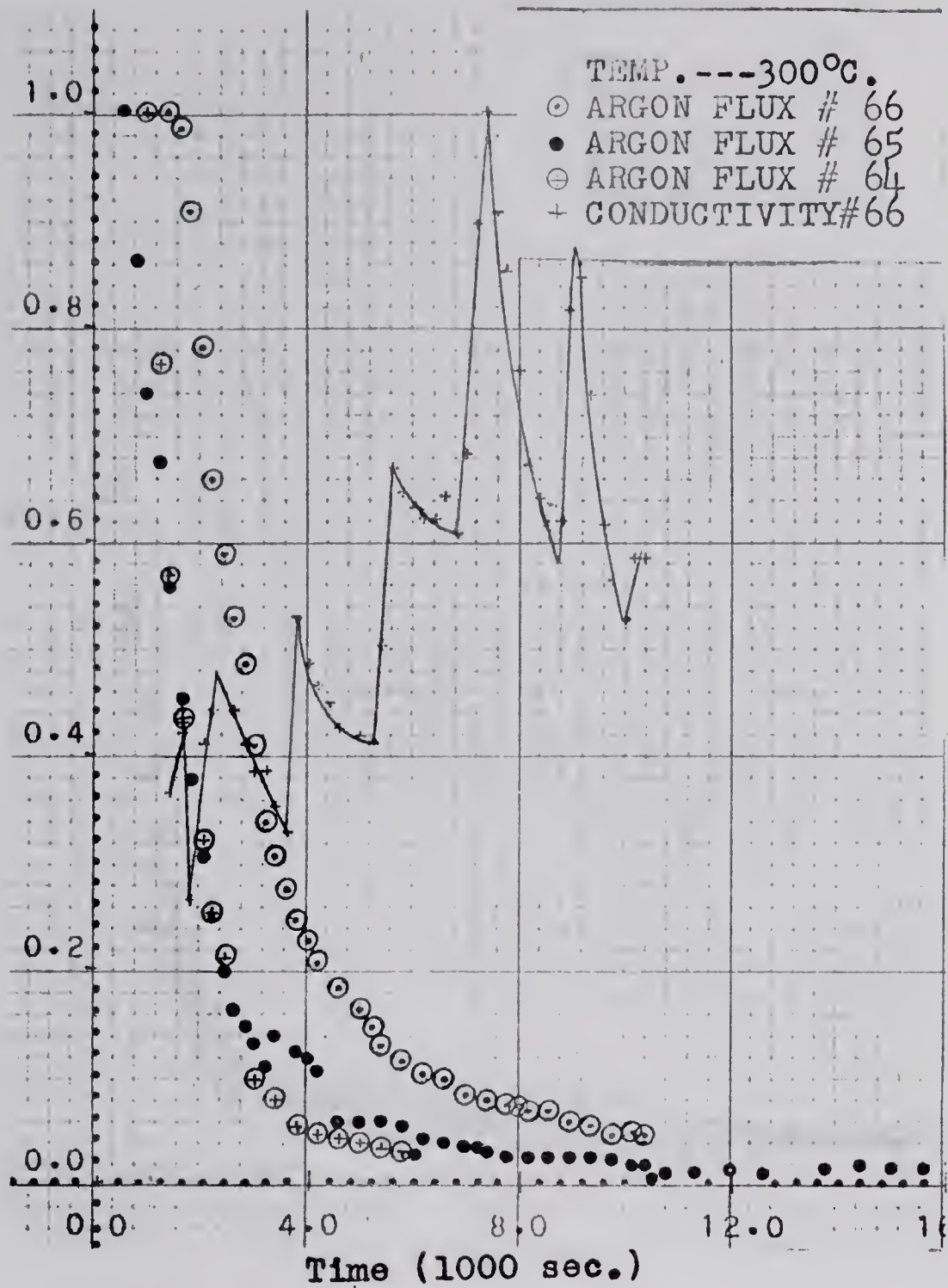


FIGURE IV-3 ARGON FLUX VS. TIME
CONDUCTIVITY VS. TIME

(Data normalized with respect to
maximum value)

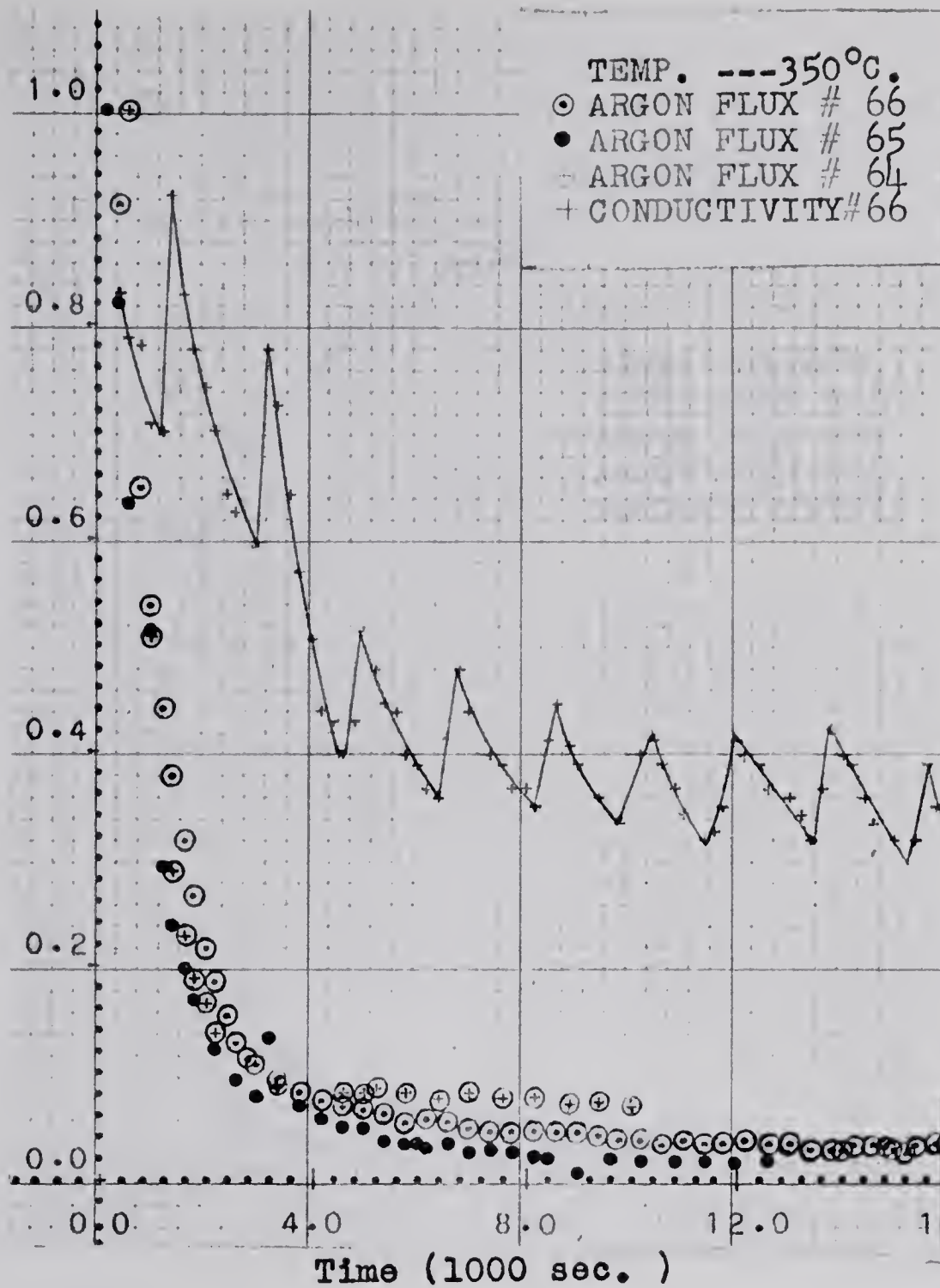


FIGURE IV-4 ARGON FLUX VS. TIME
CONDUCTIVITY VS. TIME

(Data normalized with respect
to maximum value)

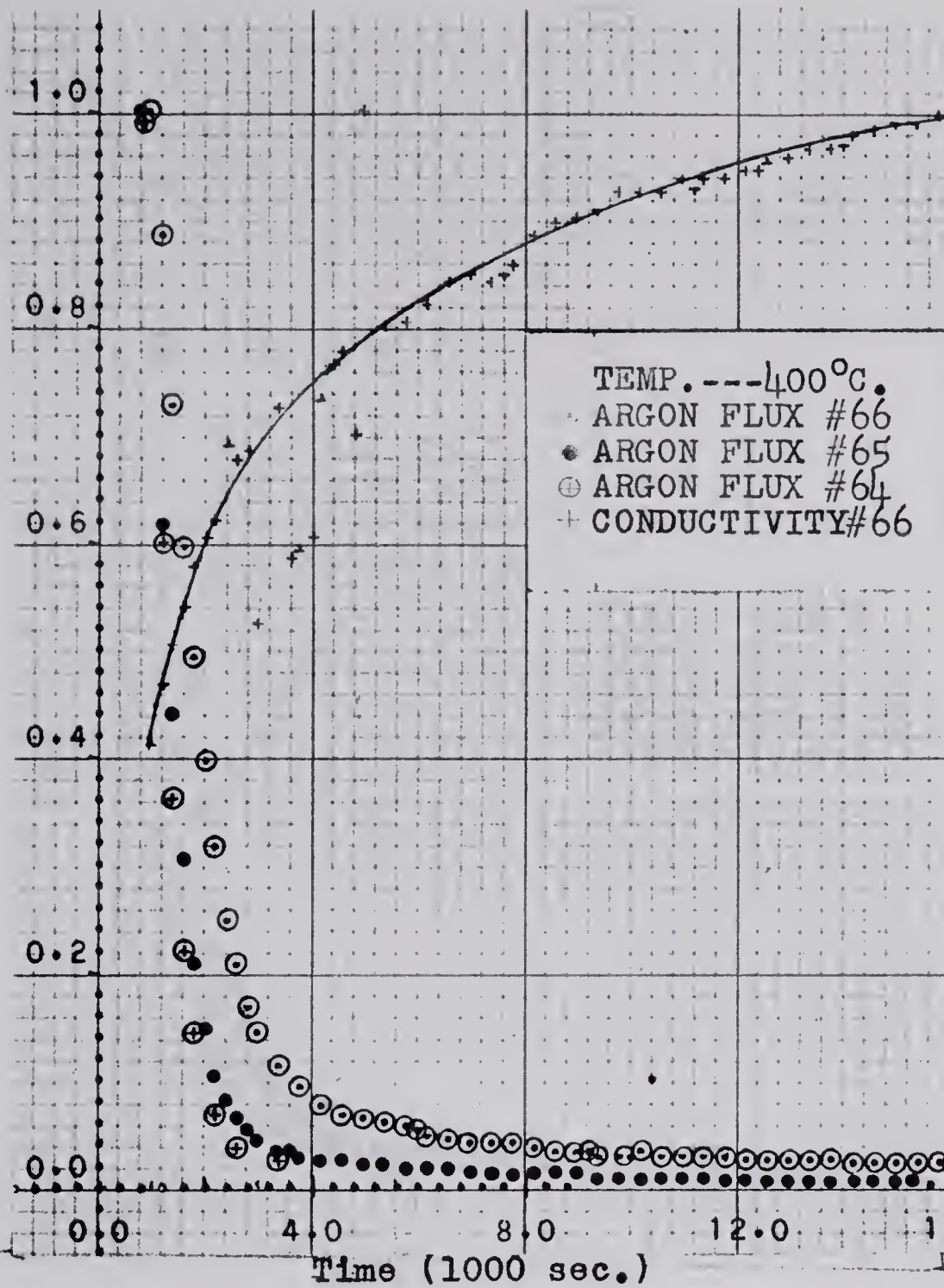


FIGURE IV-5 ARGON FLUX VS. TIME
CONDUCTIVITY VS. TIME

(Data normalized with respect
to maximum value)

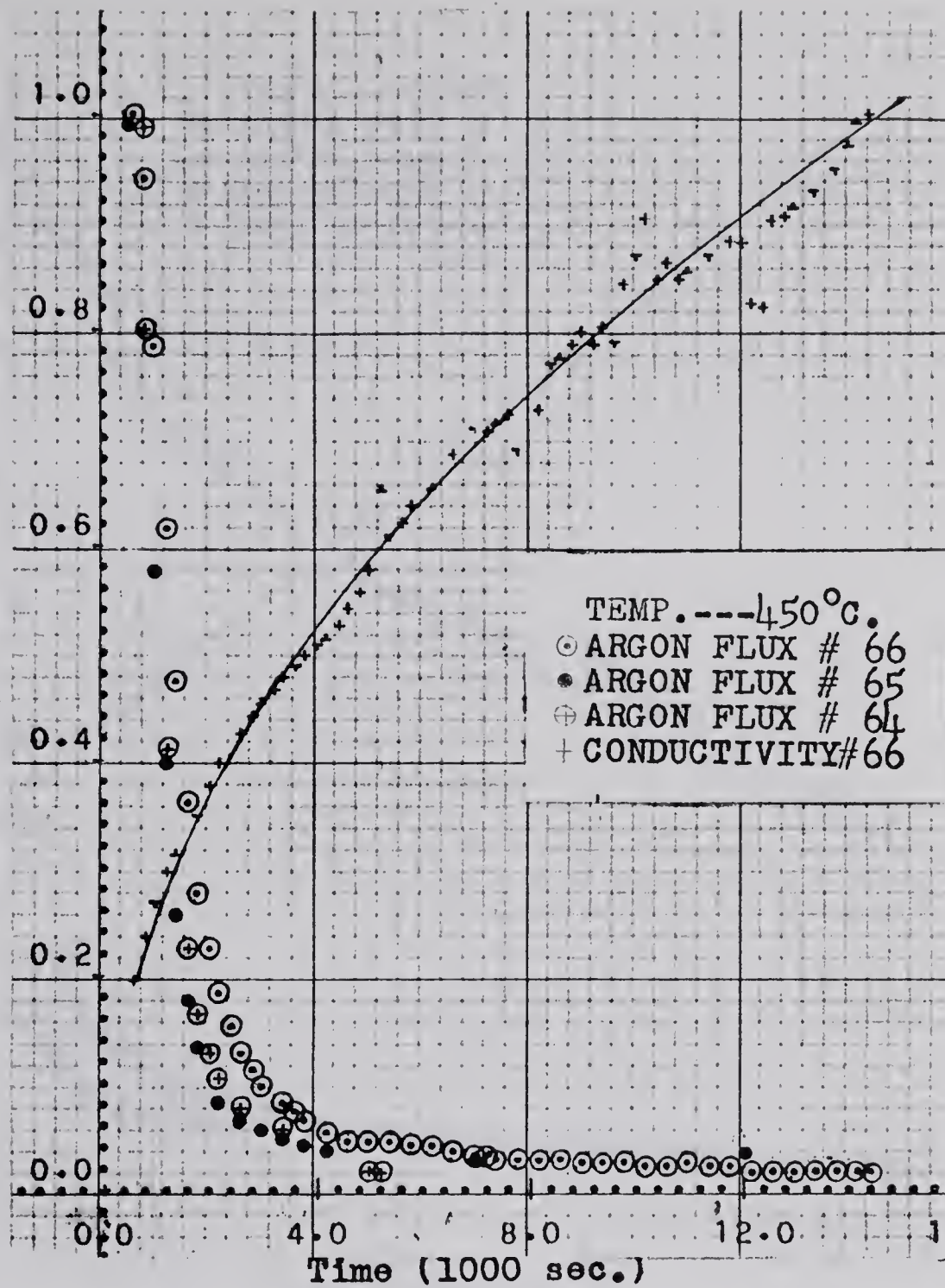


FIGURE IV-6 ARGON FLUX VS. TIME
CONDUCTIVITY VS. TIME

(Data normalized with respect
to maximum value)

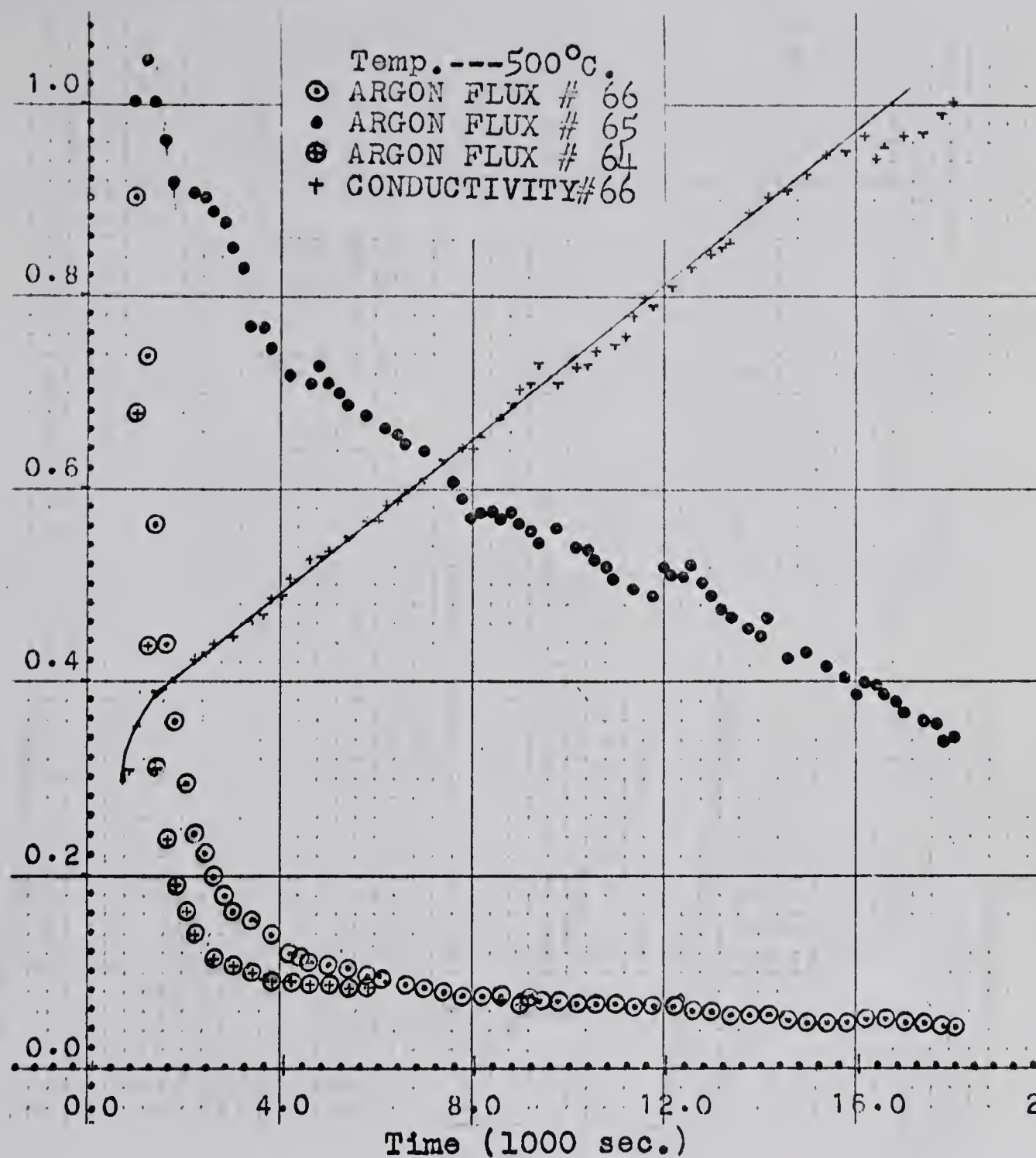


FIGURE IV-7 ARGON FLUX VS. TIME
CONDUCTIVITY VS. TIME

(Data normalized with respect
to maximum value)

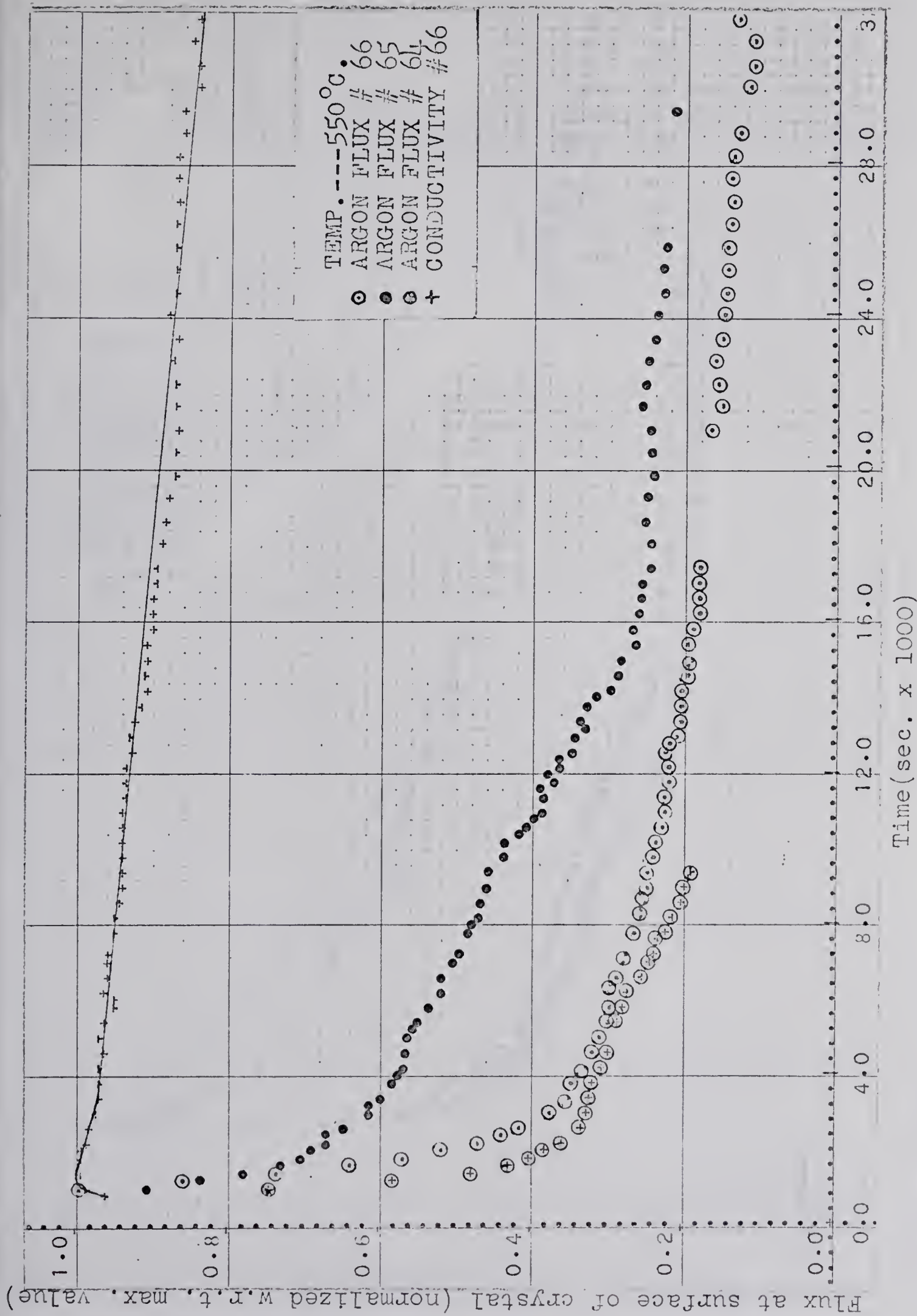


Figure IV-8

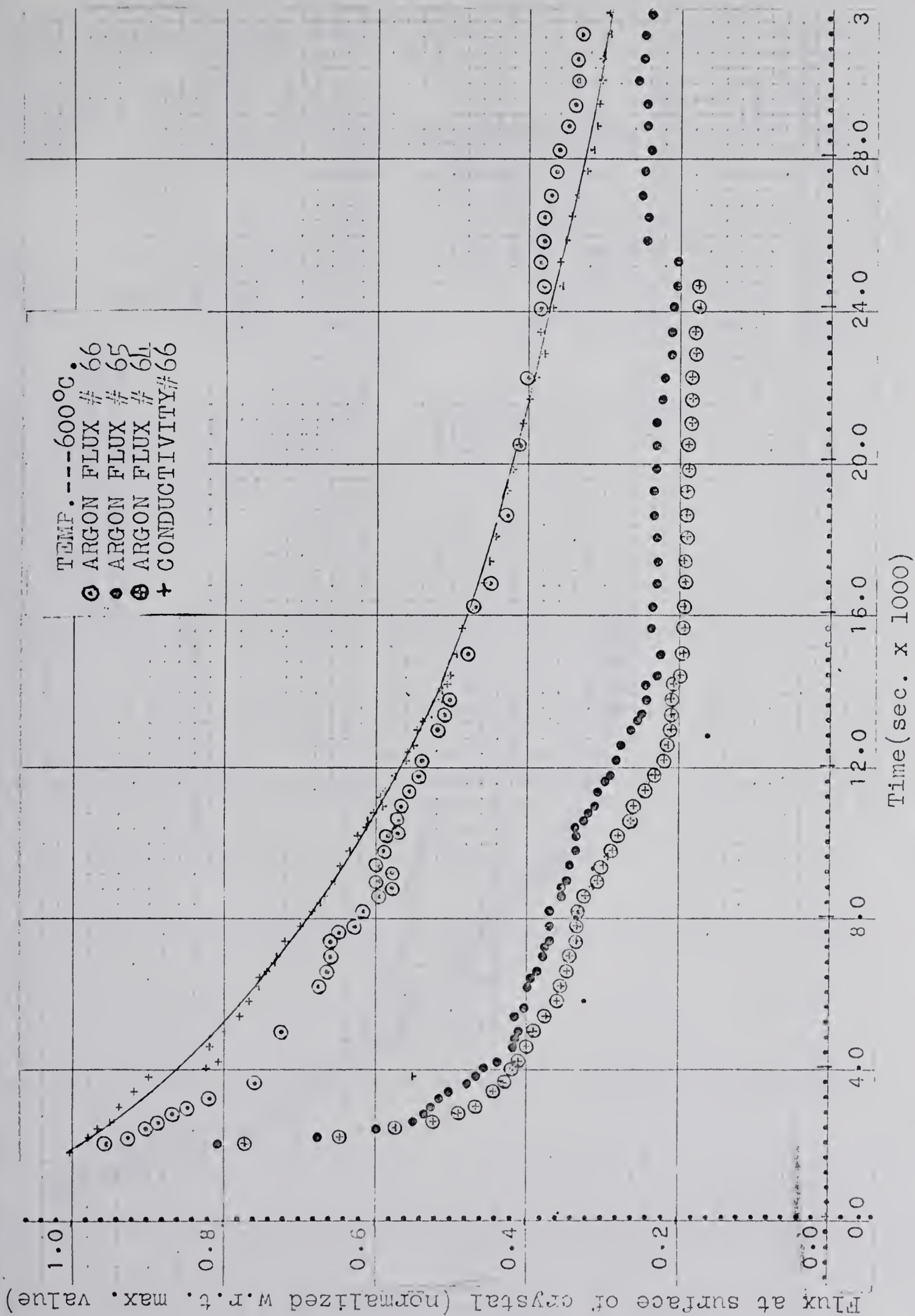


Figure IV-9

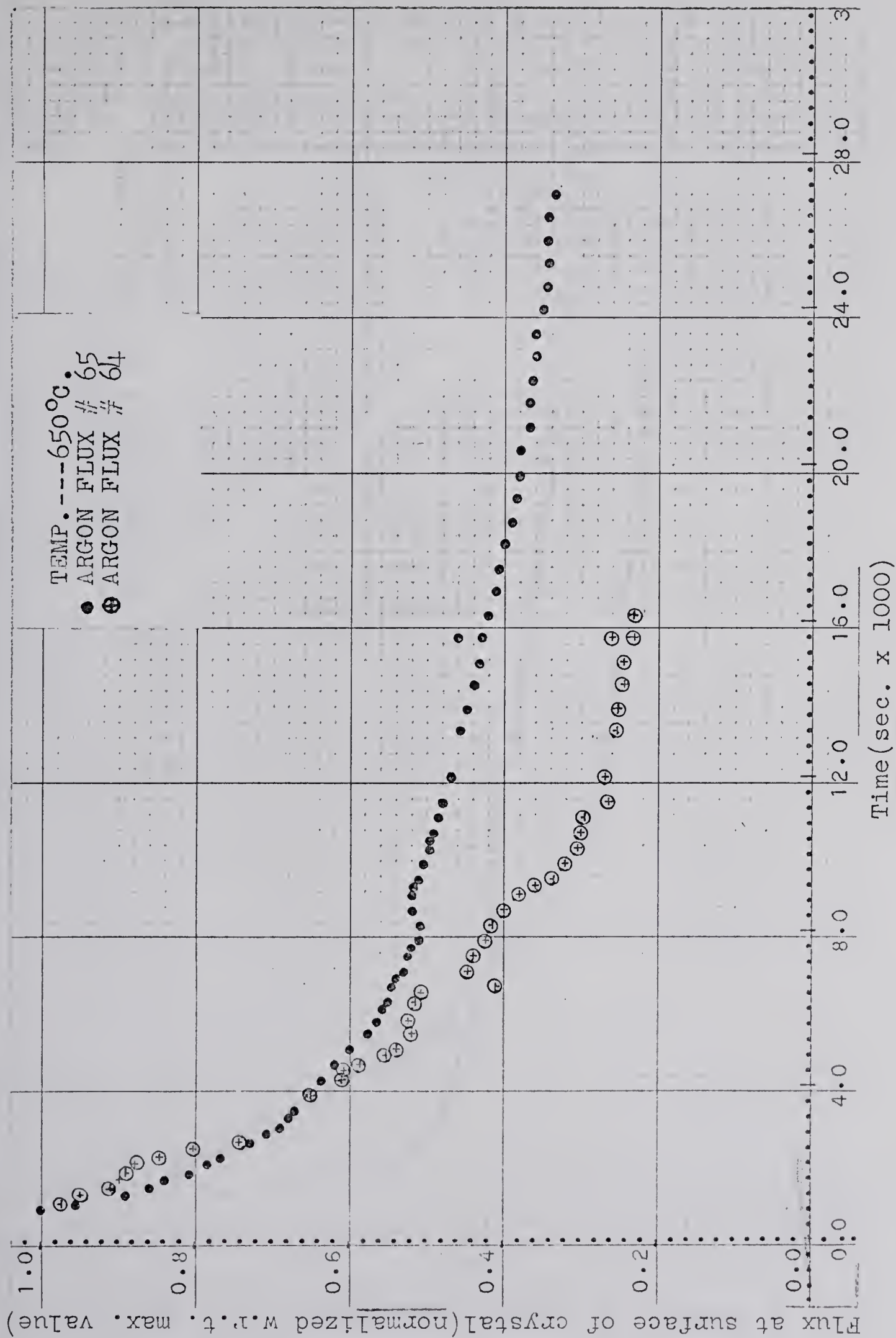


Figure IV-10

Argon Flux vs. Time
 Conductivity vs. Time

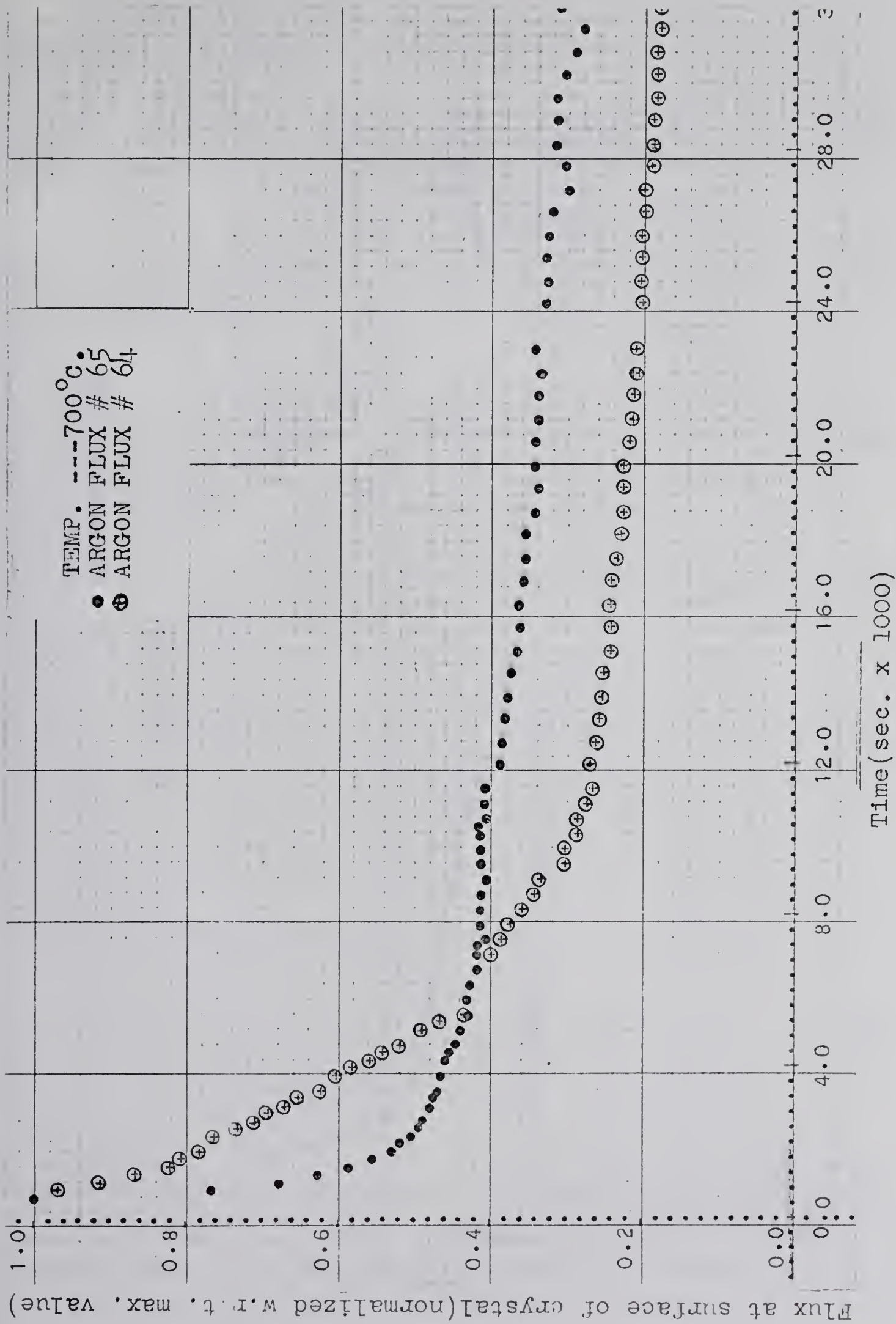


Figure IV-11

Argon Flux vs. Time
 Conductivity vs. Time

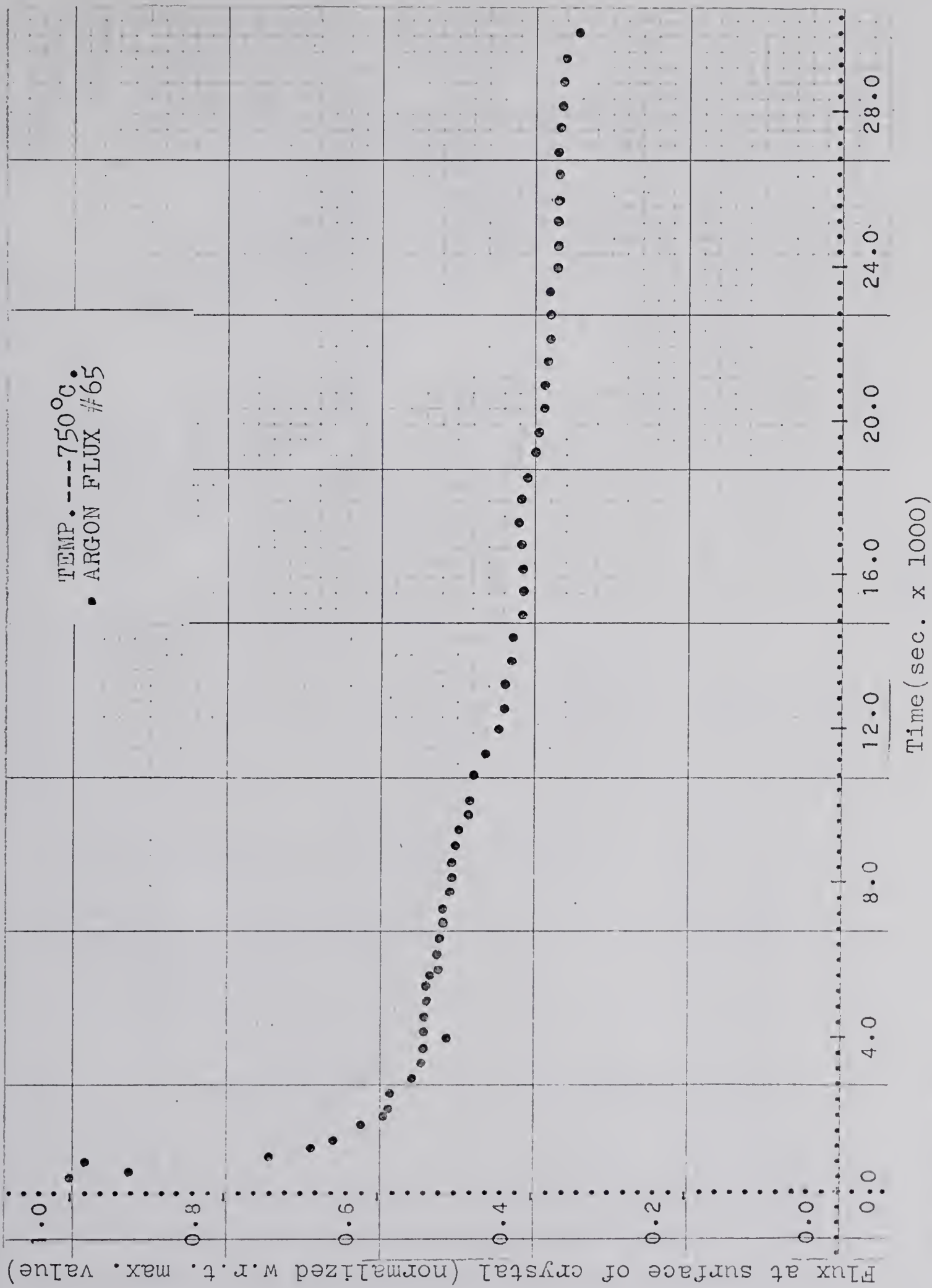


Figure IV-12

Argon Flux vs. Time
Conductivity vs. Time

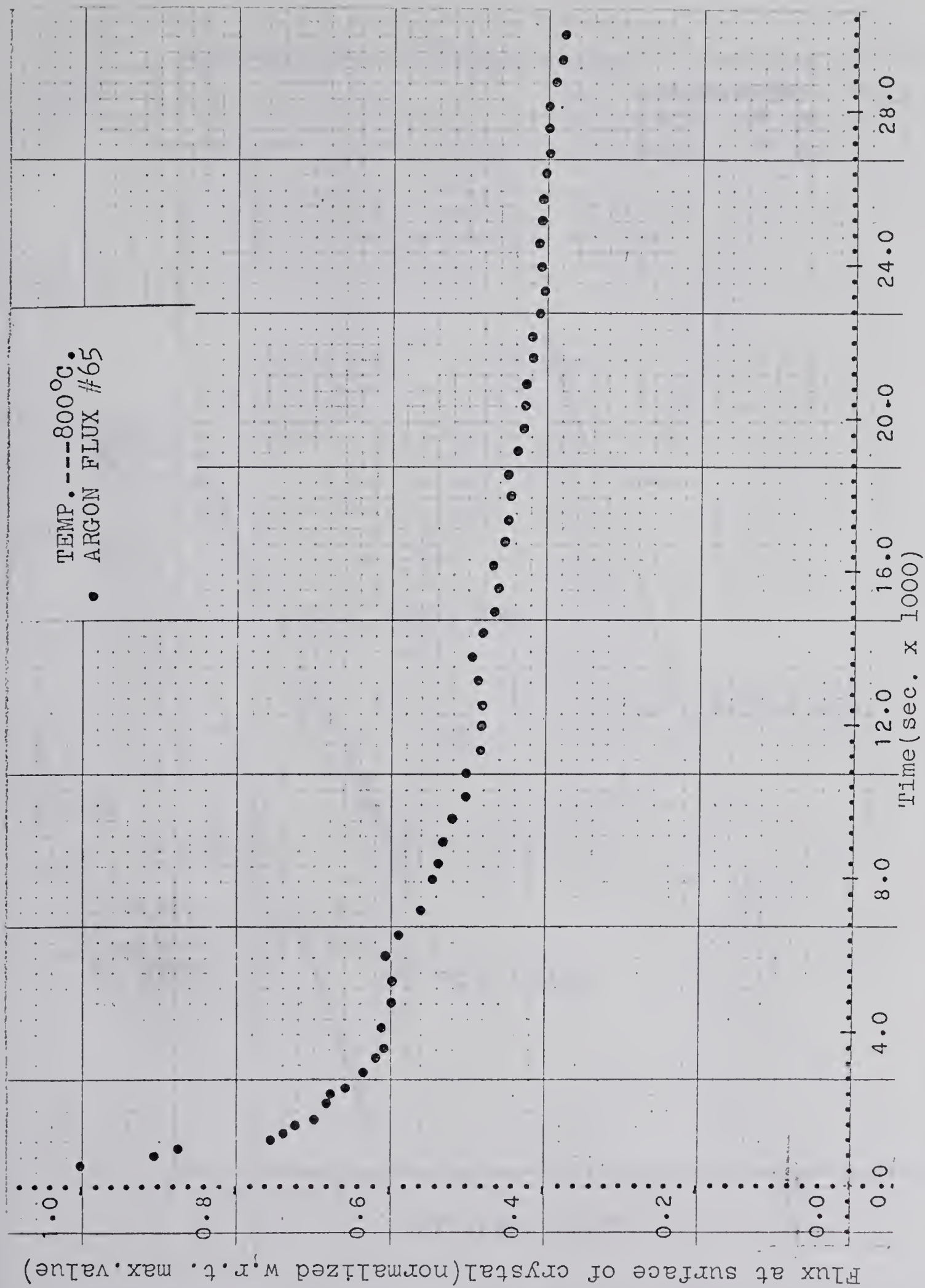


Figure IV-13

Argon Flux vs. Time
Conductivity vs. Time

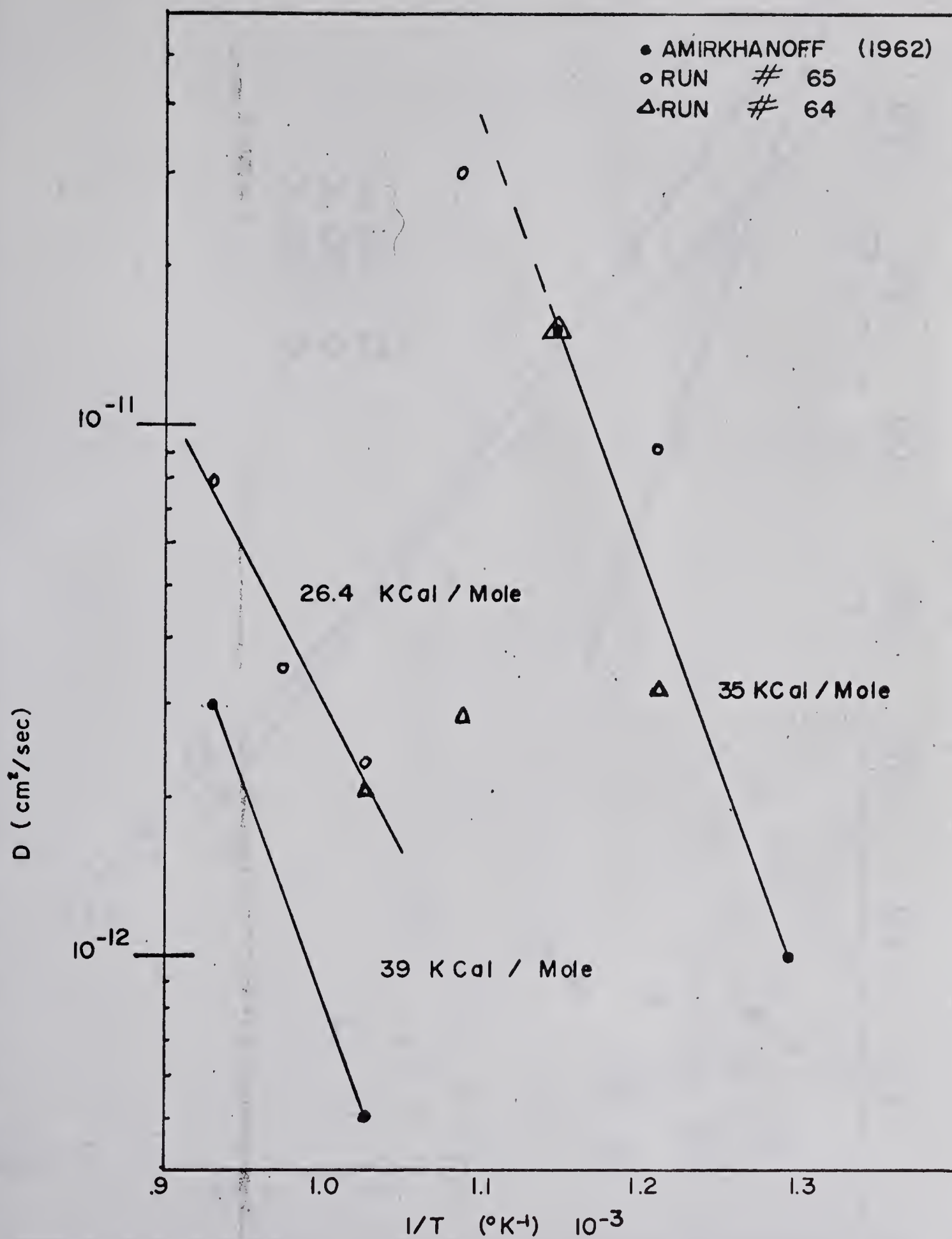


Figure IV-14. Activation Energies for Diffusion above $500^{\circ}C$; Comparison with Amirkhanoff [1961].

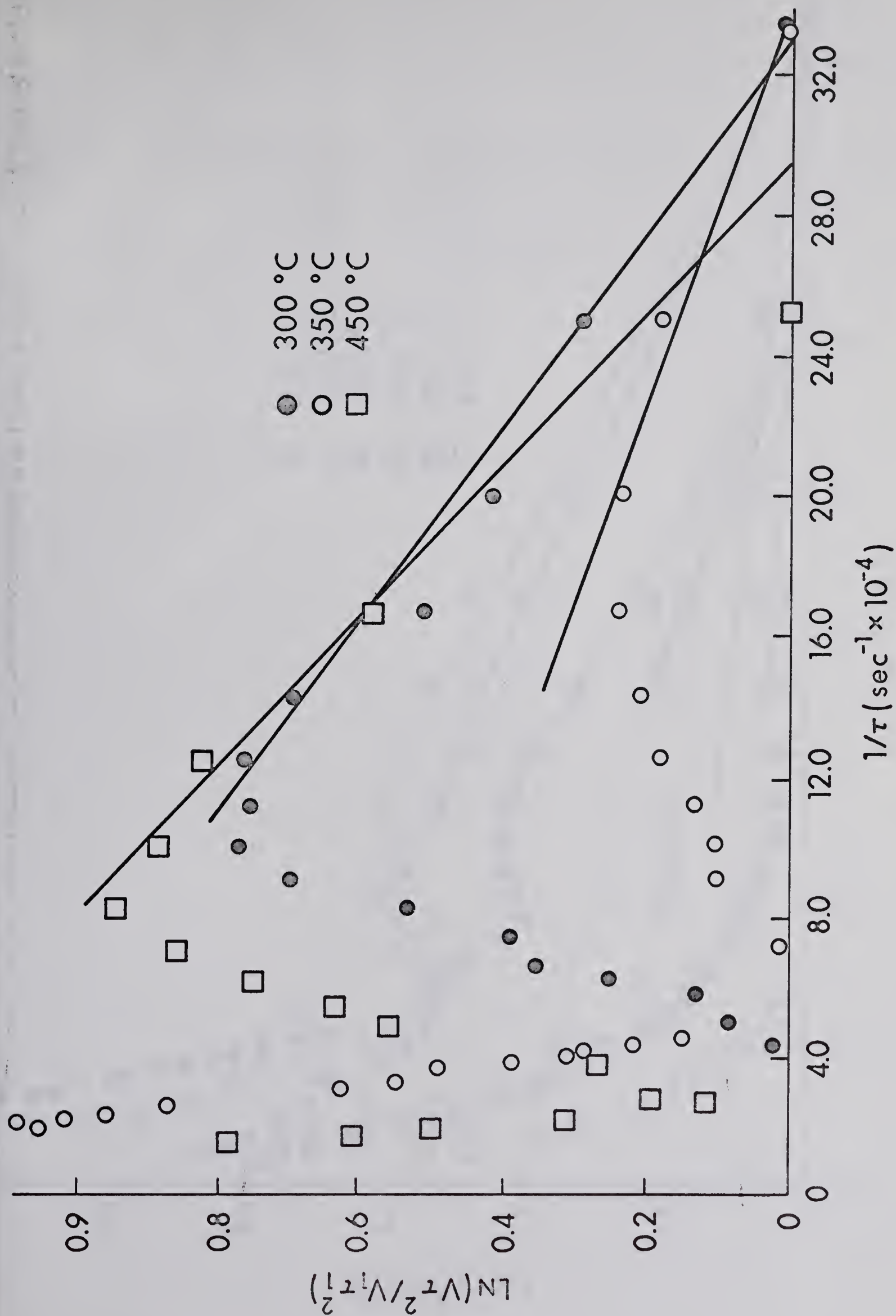


Figure IV-15. "Linearized" Flux-Time Data (experiment #61).

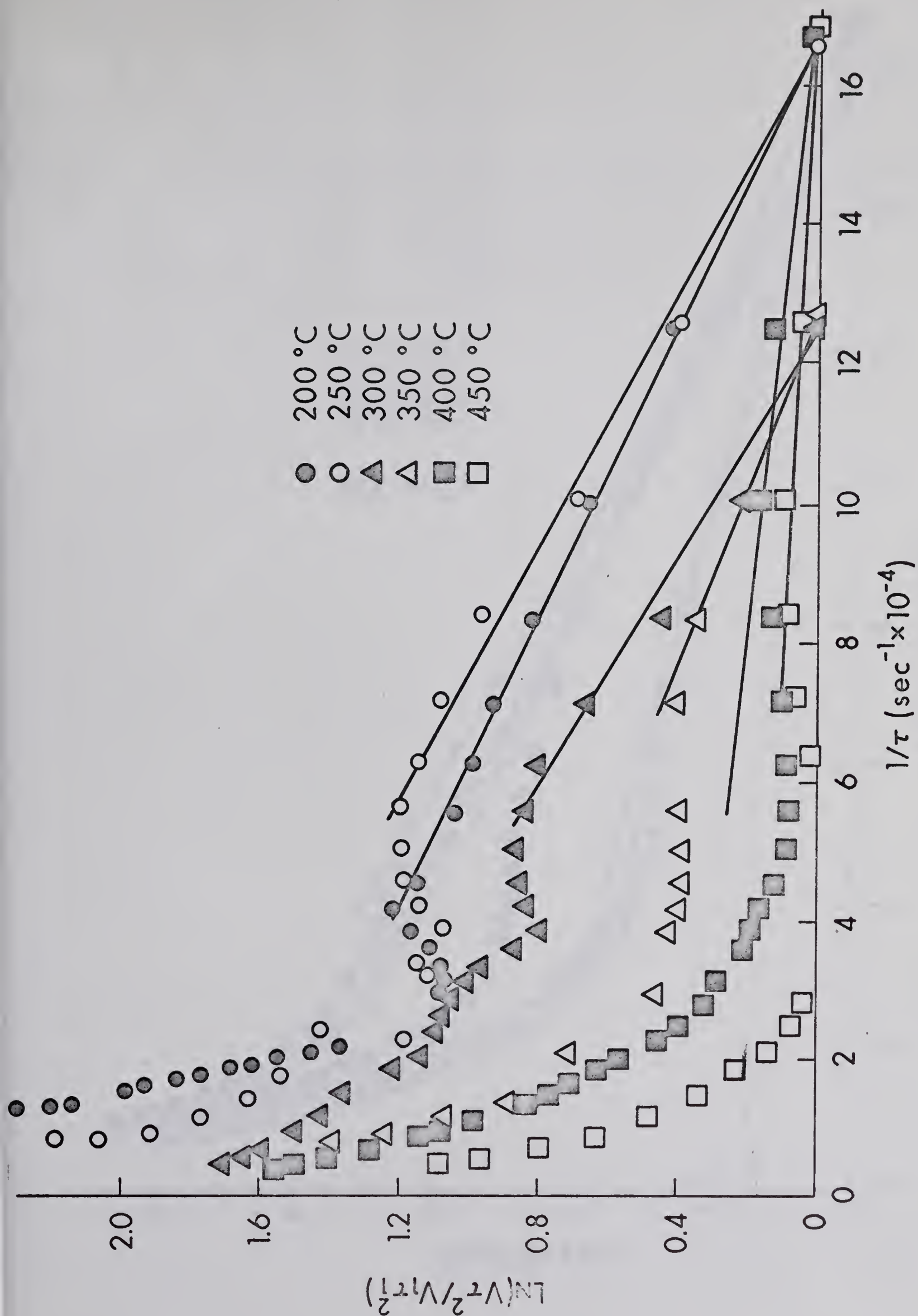


Figure IV-16. "Linearized" Flux-Time Data (experiment #65).

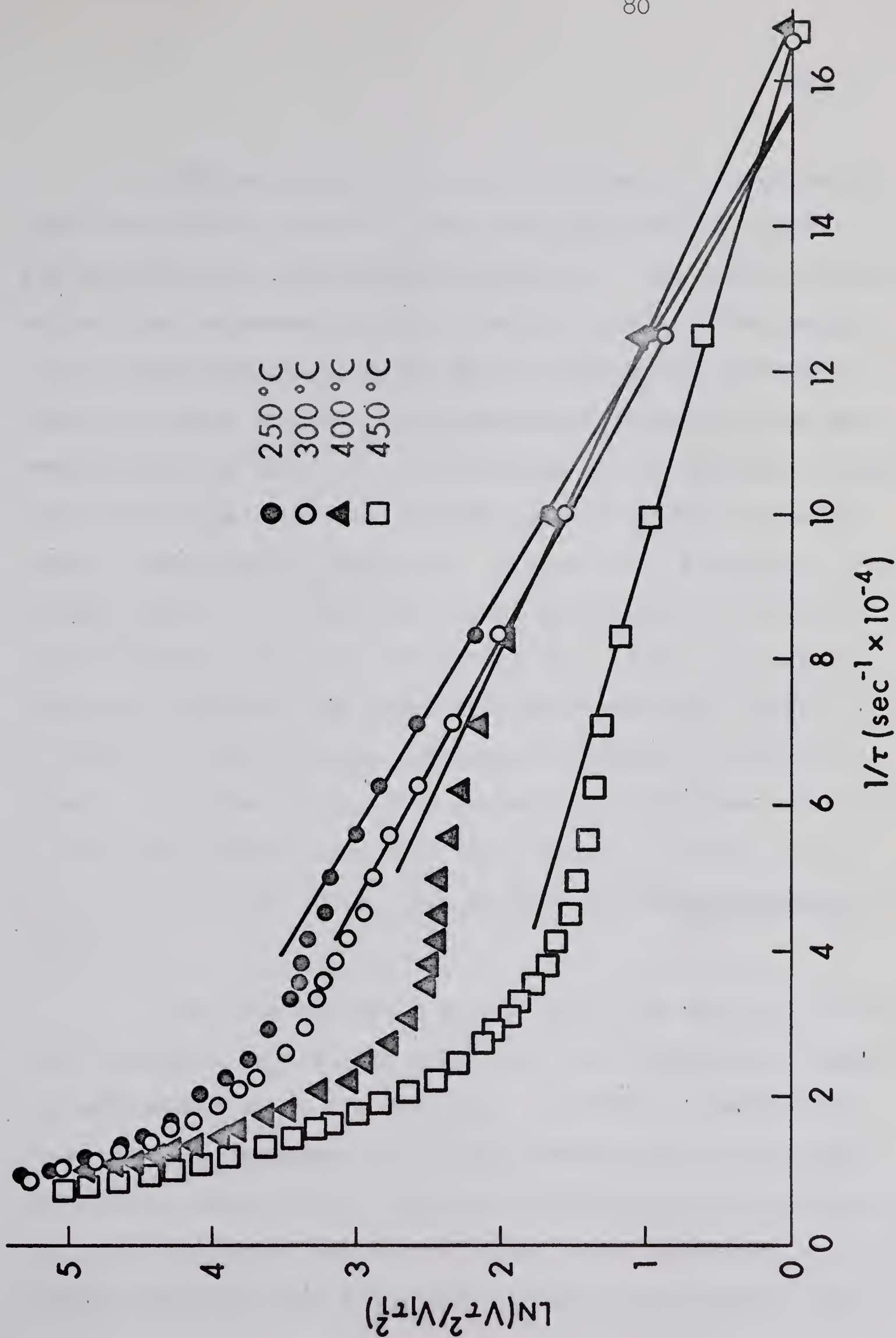


Figure IV-16 "Linearized" Flux Time Data. (Experiment #66).

Figures IV-15, IV-16 and IV-17 show the results of applying equation III-22 to the data below 500° C. Runs #64 and #65 are normal thermal diffusion. Run #66 was carried out with an impressed electric field of 2.5×10^3 volts/cm. All the experimental data for these temperatures generally follow the same pattern. The theoretical straight line plot results for the first 15 to 30 minutes of the diffusion anneal. After this time, the flux of argon begins to drop below the amount theoretically predicted. Figure IV-17 illustrates the general pattern by which the normal experimental flux time curve deviates from the theoretical one. After an initial ordinary diffusion, the argon flux decreases more rapidly than it should. This decrease continues throughout intermediate times. At longer times, this converts to a process which seems to be characterized by a much lower diffusion coefficient. It is not certain that this final portion is ordinary atomic diffusion.

The characteristic way in which the diffusion coefficient converts from a high value to a much lower one, suggests the mechanisms which are involved. It will be noted that there is an initial decrease in the flux before the low diffusion coefficient takes over. This is an important point since, if the lower diffusion coefficient were to be associated with normal diffusion from a different phase in the crystal, one

would expect the linearized flux time curve to simply make a gradual transition from the first mode to the second as the flux from the first mode went to zero. If the flux time signal were a composite of the two modes, one would expect the flux to increase in the interval of interaction rather than decrease. If there are two phases in the crystal, it would be natural to assign one diffusion mechanism to the first phase and the other to the second phase.

The second phase is observed to have a diffusion coefficient several orders of magnitude smaller than the first phase. This lowering of the diffusion coefficient cannot be attributed to the annealing of vacancies at large times, since the conductivity from 400°C to 500°C shows the dislocation density increasing with time rather than decreasing. (See figures IV-5 to IV-7). Even with the generation of point defects and vacancies, the diffusion behavior retains this intermediate decrease in flux. In fact, it is accentuated for the 400°C to 500°C temperature interval suggesting that the defects are in some way responsible for the depletion of flux in intermediate times. Baadsgaard et al [1960] and Newland [1963] have shown that sanidine, which is a disordered form of microcline, has a diffusion coefficient which is an order of magnitude lower than microcline. The disordered lattice will have a higher concentration of defects and vacancies which

for some reason cause the diffusion coefficient to be lower. This is in general agreement with the presently observed role of point defects in the argon diffusion process.

Figure IV-18 shows an Arrhenius plot of diffusion coefficient versus reciprocal temperature. Low activation energies are in effect for temperatures below 400°C . Gentner et al [1960] has observed similar low activation energies for argon diffusion in silicate minerals at these temperatures. This activation energy is observed to increase (Figure IV-14) at higher temperatures when the equilibrium concentration of vacancies is larger. This causes one to suspect that the vacancies are acting as trapping agents which establish the argon atom in a much lower potential well. At first sight, this appears contradictory since the increase in vacancies normally has the effect of increasing the diffusion coefficient. This will always be true for self diffusion, since the activation energy for diffusion through vacancies is always lower than for any other mechanism. This is not necessarily true in the case of impurity diffusion. As shown by Rimmer and Cottrell [1957], an impurity argon atom in a crystal lattice could set up considerable strain (as much as 30 ev. in copper). This lattice strain becomes extremely large for high concentrations of inert atoms and could be relieved through the capture and holding of a vacancy by the argon atom.

It seems highly probable, in view of the experimental evidence, that such trapping is taking place within feldspars. The increased vacancy concentration, caused by the phase transition, lowers the diffusion coefficient through trapping of the argon atom in vacancies or clusters of vacancies. It has been clearly demonstrated in electron microscope studies by Barnes and Mazer [1963] that the trapping of helium in copper is so pronounced and continual that large clusters of helium atoms plus vacancies form and act as nucleation sites for helium bubbles within the solid matrix. It is not being suggested at this time that such bubbles of argon form in feldspars, however, the possibility of this happening should not be ignored. The time dependence of helium diffusion in aluminum [Glyde and Mayne 1965] bears strong similarity to the diffusion of argon in feldspar. It is known that strong trapping and bubble condensation occur for helium in aluminum. The controlling factors in this are the concentration of the inert gas (i.e., it must be in excess of the saturation amount) and the concentration of vacancies [Barnes 1960].

If a trapping mechanism is postulated for the behavior of argon diffusion in feldspars, the drop in flux at intermediate times is accounted for, as are the anomalies in the argon retention which have been observed in geochronology

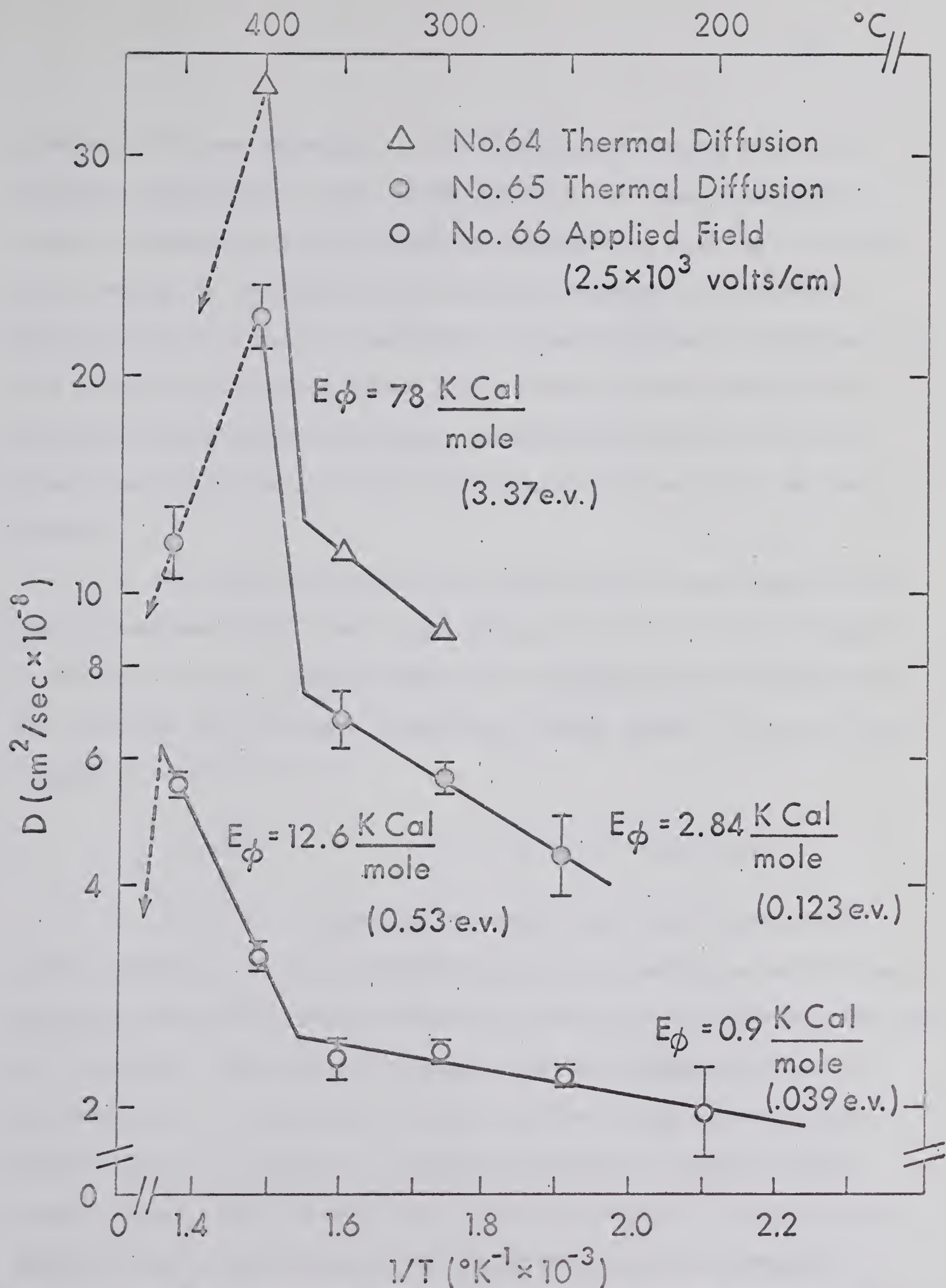


FIG IV-18 LN(D) vs. $1/T$ for thermal diffusion and diffusion under conditions of Applied Electric Field.

studies of these minerals. The highly disordered state of feldspar supplies a large concentration of vacancies which trap the argon atom with binding energies as high as 70 to 90 K Cal/Mole, as evidenced in diffusion studies of sanidine. This does not occur in the highly ordered state of feldspar and the diffusion of argon takes place with the low activation energies associated with grain boundary diffusion and other planar defects such as twin planes and intersections of twin planes.

The time at which the experimental data depart from its linearized flux time curve (Figures IV-14, IV-15, IV-16) indicates how the concentration of trapping sites increases as the maximum of the phase transition takes place. The diffusion length is defined as

$$L \equiv \sqrt{Dt'}$$

D = diffusion coefficient

If t' is chosen as the time when the experimental curve departs from the theoretical one, an estimate of the mean distance which the argon atom must travel to a trapping site may be obtained. This is an average distance indicating how far the majority of atoms must travel before trapping commences. Figure IV-19 is a plot of trapping diffusion length versus temperature. The conductivity curve of Figure IV-5 indicates that at 400° C the density of vacancies begins increasing

rapidly due to the transition. It is at this temperature that the diffusion trapping length minimizes indicating that the density of vacancies are responsible for the trapping of argon atoms in feldspar. The minimization of trapping length at this temperature means that the argon atom moves a minimal distance before being trapped as compared to lower temperatures where the density of vacancies is lower and the trapping length longer. The electric field is seen to generally lower the trapping length but does not affect the position of the minimum. This can be interpreted in terms of the electric field moving vacancies to the argon atoms in addition to these atoms moving toward the vacancies, thus lowering the time required for the trapping to take place. For further discussion as to how this information may be used to arrive at a model for the trapping mechanism reference is made to Glyde and Mayne [1965]. This same article discusses possible reasons for the increase in trapping length with temperature (as occurs after 400°C). A balance between the generation rate of vacancies (as determined by its activation energy) and the trapping rate (determined by diffusion coefficient, concentration, and lattice structure) is thought to be responsible for this increasing trapping length.

As mentioned in part B of this section, the data above 500°C require the use of equation III-6. A plot of flux versus reciprocal square root of time should be linear, however,

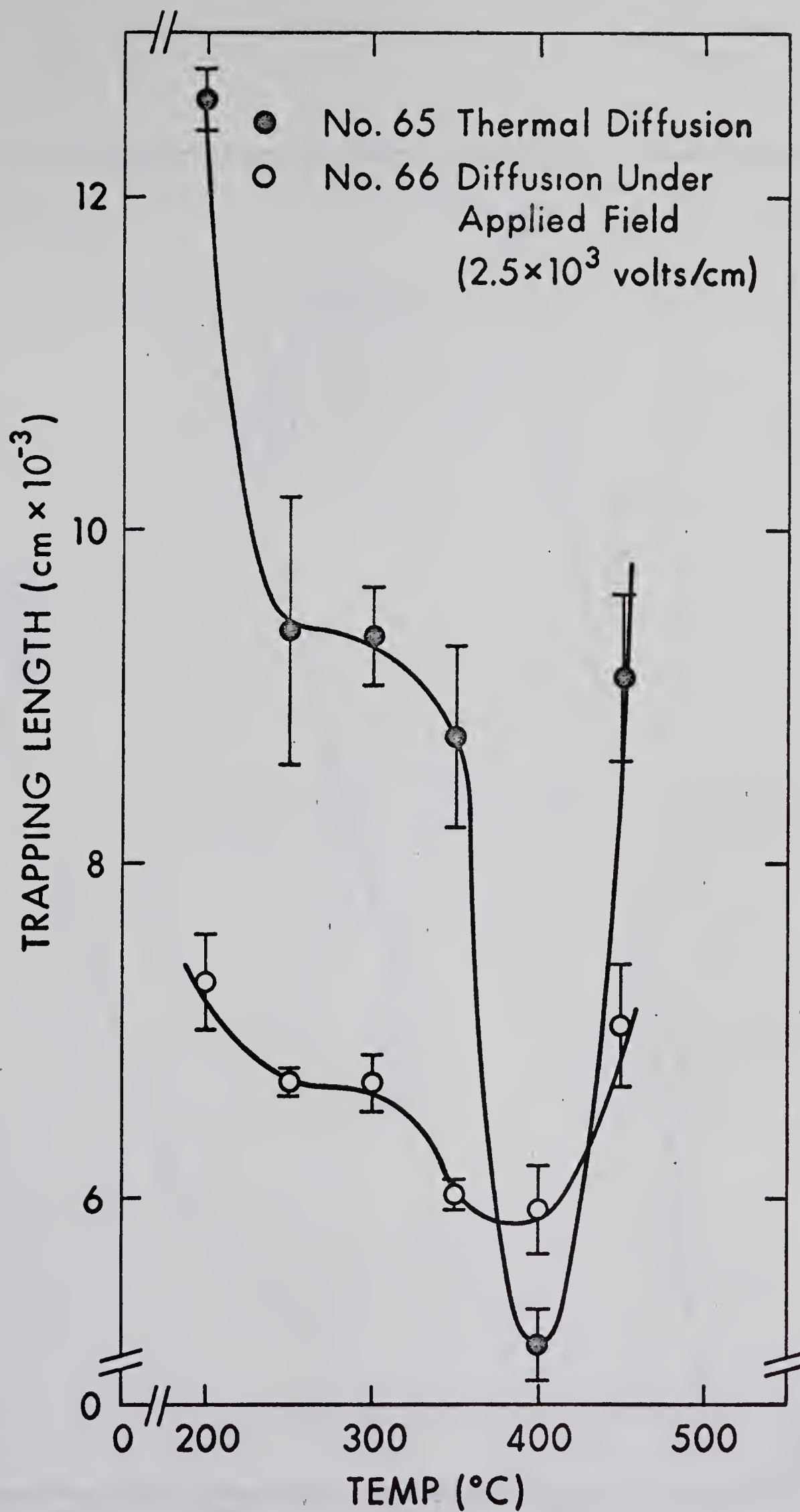


Figure IV-19 Diffusion length to traps as a function of temperature.

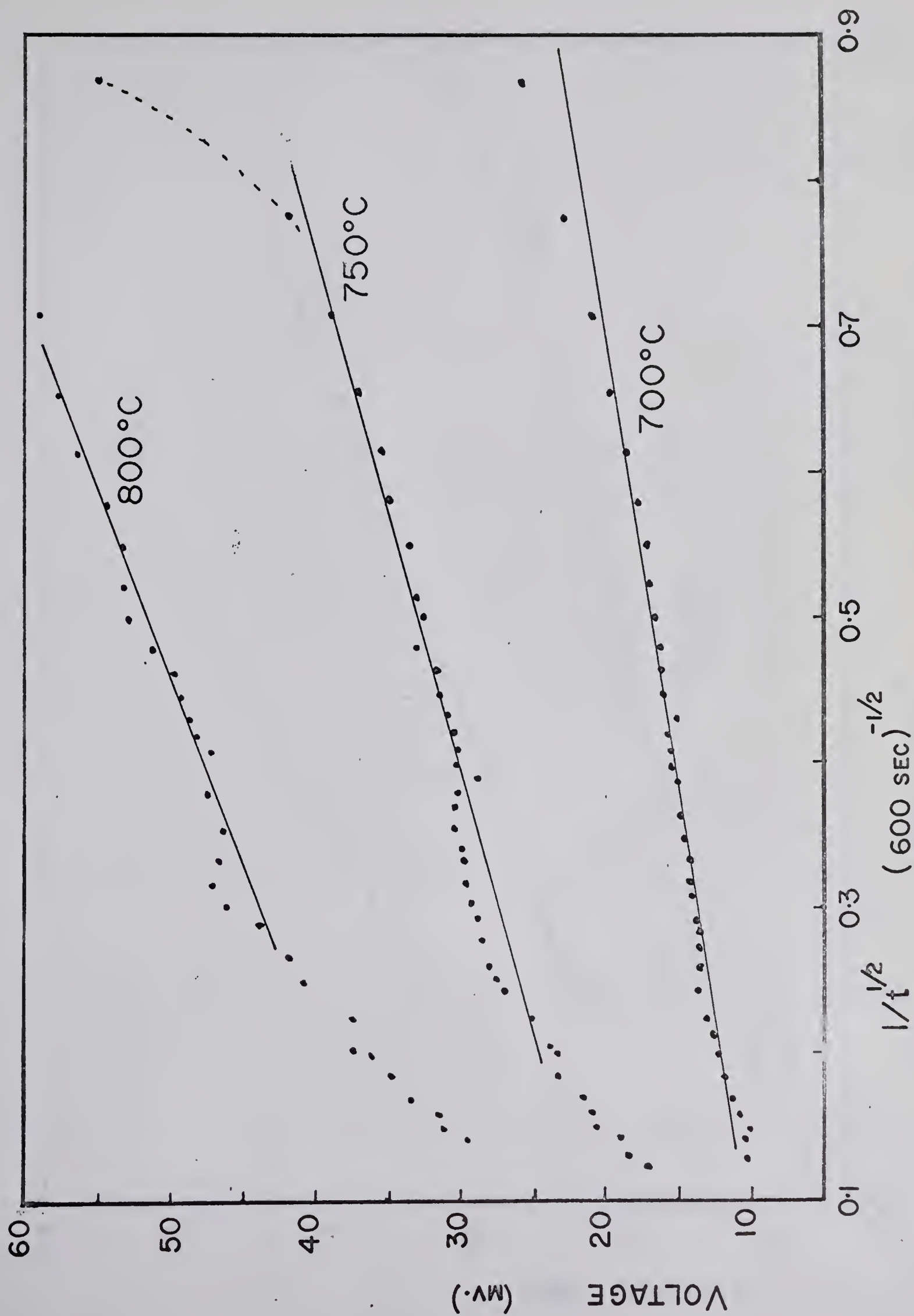


Figure IV-21 Mass Spectrometer Output vs. $1/t^{1/2}$ (700°C to 800°C)

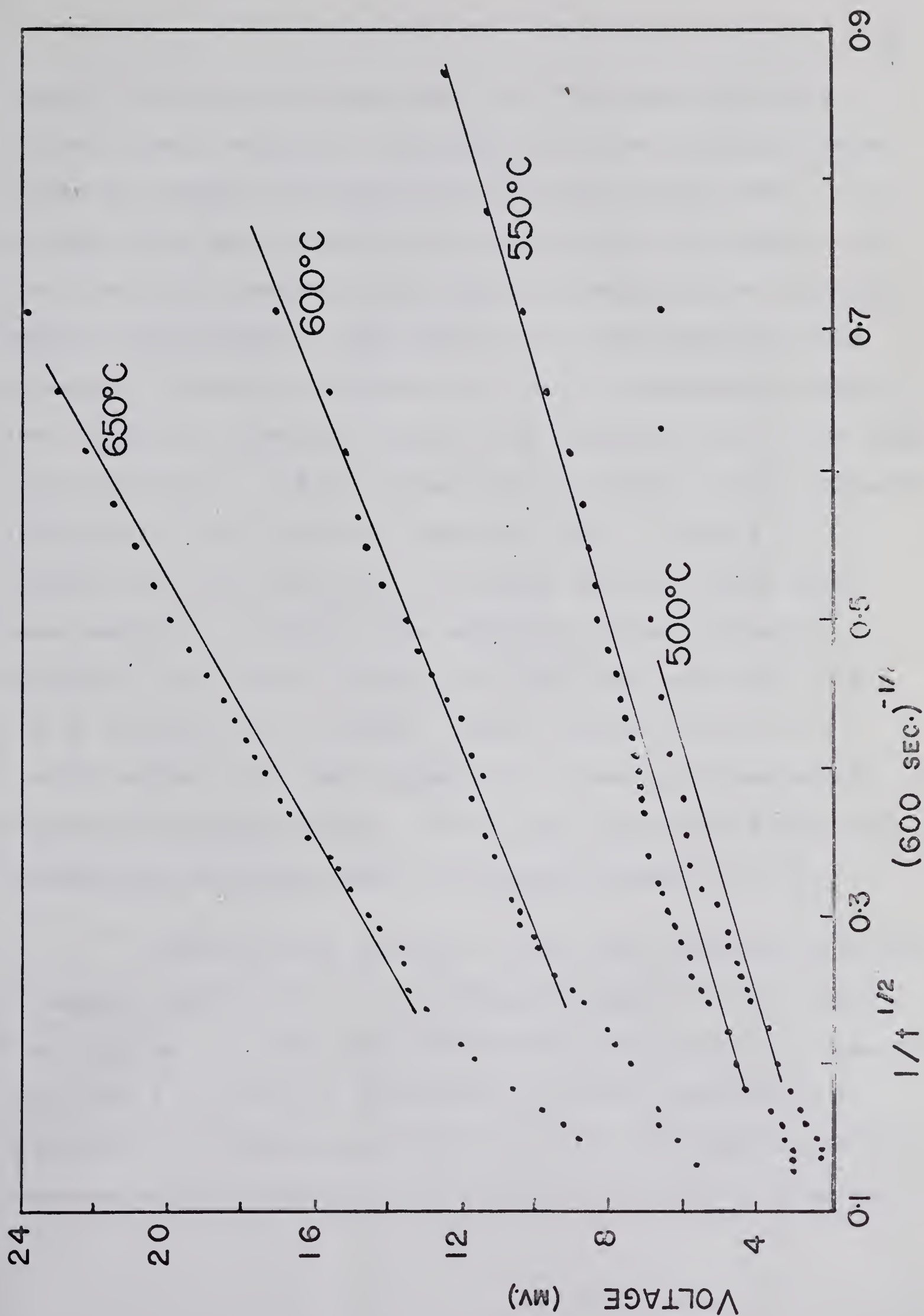


Figure IV-20 Mass Spectrometer Output vs. $1/t^{1/2}$ (500°C to 650°C)

figures IV-20 to IV-21 show that the flux falls below any initial linear behavior. In calculating the slopes of these curves, an average straight line was drawn through them. If a straight line were fitted to the initial low time portion of the curve, one observes a flux which decreases below the value which it should have. This behavior is consistent with the concept of trapping introduced for the low temperature data. Hart [1960] has observed similar time dependence of the Ar flux from microcline. His data show that the amount of gas released continually falls below its expected value. Studies of krypton and xenon diffusion in uranium dioxide [Hurst 1962] have resulted in similar time dependent release patterns. Theories involving the trapping of gas atoms have been motivated by results such as these. These theories allow for a process whereby the inert atoms are trapped and subsequently released from these traps. Hurst [1962] has applied this idea successfully in explaining the release of xenon from UO_2 .

The following analysis of the time dependent diffusion of argon in microcline is an attempt to simplify this concept. The trapping and subsequent behavior may be explained by associating with a continually decreasing diffusion coefficient a continually increasing activation energy. The trapping is then represented by a transition of the diffusing atom to a deeper

potential well. The rate at which this happens is determined by the rate at which the activation energy changes. It shall be assumed that the diffusion is an activated process and the Arrhenius equation is applicable throughout, i.e.,
 $D = D_0 \exp(-E/KT)$. The activation energy E is a function of the time and therefore the diffusion coefficient D shall be a function of the time as well. D_0 will be assumed a constant, K is Boltzmann's constant, and T is the absolute temperature.

The trapping represents a lower potential energy state for the argon atom, and the following model is proposed to suggest a mechanism by which this happens. The ideas are based on the concepts of Rimmer and Cottrell [1957] in their theoretical consideration of the solution of inert gases in copper.

When the potassium atom converts to argon by K-capture, the electron cloud around the argon nucleus will expand due to the loss of one positive nuclear charge. This loss of a plus one charge also creates a negative electrical imbalance at the site of the argon atom. This charge imbalance will repel the electron cloud of the negative ions around it and at the same time attract the positive ions. The combination of these effects sets up a strain condition within the lattice. This strain is principally due to the absence of electrostatic charges on the part of the inert gas atom and results in the

solubility of inert gases in solids being very low. If the amount of argon in the lattice exceeds its solubility limit, it is reasonable to expect the total strain of the lattice to become quite large. It is difficult for a positive ion to get into the site occupied by the argon atom because it must force the inert gas atom into an interstitial position which can result in an even greater strain energy. (The strain caused by an inert gas atom being in an interstitial position is usually much greater than if it is present substitutionally). A mechanism by which this strain can be released, is to have a vacancy attach itself to the site of the argon atom and allow the ions around this volume to relax into the vacancy. This capturing of a vacancy represents a lower potential energy state for the argon atom.

Consider a situation where the number of argon atoms in the lattice exceeds the amount which could be contained in the lattice under ordinary circumstances. This shall be referred to as a supersaturated condition. It shall be supposed that at any time, the total strain energy of the lattice is proportional to the number of particles in excess of the saturation limit. (Strain due to trapped atoms will be considered as negligible).

$$E_{\text{strain}} = \gamma(N - N_p) \quad (\text{IV-2})$$

N = number of untrapped argon atoms in the lattice at some time " t ". N_p = number of untrapped argon atoms that can be dissolved in the lattice without significant macroscopic strain.

The above equation assumes only one lattice site for the untrapped atoms, and one site for the trapped atoms. (This can be simply extended by summation to include the existence of more than one site). Let E_s be the total strain energy of the lattice. The change in E_s with respect to time will be,

$$\frac{\partial E_s}{\partial t} = \frac{\partial E_s}{\partial N} \frac{dN}{dt} \quad (\text{IV-3})$$

Let the trapping rate $\frac{dN}{dt}$ be determined by the number of atoms in excess of the saturation limit. Then,

$$\frac{dN}{dt} = \lambda(N - N_p) \quad (\text{IV-4})$$

The solution of this differential equation is an expression for the number of untrapped atoms in the lattice as a function of the time. This will be:

$$N = N_p + (N_o - N_p)e^{-\lambda t} \quad (\text{IV-5})$$

where N_o is the number of untrapped atoms at time $t = 0$ and λ is a quantity which should be related to the density of vacancies in the crystal and their diffusion rate.

The strain energy per particle (whether it is in excess of the saturation limit or not) is given by the constant γ . (Rimmer and Cottrell [1957] suggest a method for calculating this quantity).

$$\text{Since } \frac{\partial E_s}{\partial N} = \gamma, \quad (\text{IV-6})$$

substitution of (IV-4) and (IV-6) into (IV-3) gives the following expression for the change in total strain energy with time:

$$\frac{\partial E_s}{\partial t} = -\gamma \lambda (N - N_p) \quad (\text{IV-7})$$

Substituting for N from equation (IV-5) gives

$$\frac{\partial E_s}{\partial t} = -\gamma \lambda (N_o - N_p)e^{-\lambda t} \quad (\text{IV-8})$$

Integrating this gives:

$$E_s = -\gamma \lambda (N_o - N_p) \int_0^t e^{-\lambda t} dt$$

The total strain energy, which is the result of supersaturating the lattice, is:

$$E_s = \gamma (N_o - N_p) e^{-\lambda t} + C. \quad (\text{IV-9})$$

where C is the constant of integration.

At $t = 0$, $E_s = \gamma (N_o - N_p)$ and therefore $C = 0$.

Therefore, the strain energy as a function of the time is given as

$$E_s = \gamma (N_o - N_s) e^{-\lambda t} \quad (\text{IV-10})$$

λ determines the rate at which strain is released through trapping only. This equation in no way accounts for the strain release due to diffusion loss of argon atoms from the lattice.

Equation IV-10 represents the complete lattice strain. This is a summation of the effects from all argon atoms. It is interesting to determine whether the strain fields of individual argon atoms overlap. There are 10^{14} atoms/cc. of argon in the crystal lattice. The volume per atom is then 10^{-14} cc./atom. The radius associated with this volume is $1330 \text{ \AA}$. This will be the mean distance between argon atoms.

The theoretical work of Rimmer and Cottrell indicated that the strain of a single atom within the lattice of copper did not extend beyond second nearest neighbors or approximately $8 \text{ \AA}$. The results of nuclear magnetic resonance studies, on lattice distortions around impurity ions in alkali halide crystals, indicates that there can be as many as 140 neighboring atoms affected by an impurity. [Fukai, 1963]. Generally, the quadrupolar field effects on resonance lines drops off as $1/r^3$ and have negligible contribution beyond $20 \text{ \AA}$ from the impurity centre. This indicates that the $1330 \text{ \AA}$ between argon atoms will be large enough so that their strain fields do not overlap.

Since the argon atoms do not act in a collective way, one can consider the trapping to be a statistical process, where the number which are trapped depends on the number available for trapping. Equation IV-10 is the result of such an assumption.

If these atoms may return to the diffusion process from their trapping sites, one can set up a differential equation which will take into account the following three processes. (1) diffusion from the lattice, (2) trapping, (3) return from these traps. This will result in the following diffusion equation:

$$\frac{\partial c}{\partial t} = D \nabla^2 c - \lambda(c - c_p) + mb$$

C is the concentration, C_p the concentration at saturation, D the diffusion coefficient, λ the trapping rate, m the concentration of atoms in traps, and b the probability of an atom getting out of a trapping site. Hurst [1962] has made an analysis of such a diffusion process. He applied it to anomalous xenon diffusion in UO_2 and was able to account for certain deviations from simple diffusion.

In addition to the mechanisms introduced by Hurst, one must also be aware of the possible migration of an entire trapping site which contains the argon atom. It has been shown by Geguzin and Ovcharenko [1966] that gas inclusions in NaCl can be made to migrate under the action of an applied electric field. This means that it is physically possible for the entire trapping site which contains the gas to move through the bulk of the crystal. This could be a possible mechanism for the diffusion of argon at high temperatures. The conductivity curve of Figure IV-9 is seen to be nearly identical in form to the gas release curve. This could mean that as vacancies arrive at the surface they release the argon which they contain and then remain at the surface no longer participating in the conduction process.

CHAPTER V. EXPERIMENTAL CONDUCTIVITY CURVES

During run #66, the electrical conductivity of the crystal was simultaneously recorded with the diffusion data. The results are presented with the experimental flux-time curves of Chapter IV. (Figures IV-1 to IV-7). The general behaviour of the conductivity suggests that it be broken into three major groups according to whether it is above or below certain critical temperatures. The first group is in the temperature range from room temperature to 350°C . In this range the conductivity is probably semi-conduction. The next range is the one hundred degree interval between 400°C . and 500°C . where the conductivity increases monotonously with the time. The final range is above 500°C . where the conductivity decreases monotonously with the time.

(A) Temperatures below 350°C .

The conductivity below 350°C . is rather anomalous and evades simple explanation. It has small, but clearly observable, oscillations with the time. In addition, there can be a general increase or decrease in the overall curve. The oscillations have a characteristic period of about twenty minutes and are not symmetric about the maximum and minimum amplitude. The increasing part of the half cycle has a steeper slope than the decreasing part.

One's first reaction is to attribute this oscillation to the measuring circuit. It would not be difficult to imagine the crystal sample acting as an insulating capacitor in the measuring circuit and alternately building up surface charges and dissipating them. This could be accomplished through interaction with a possible space charge of gas between the electrodes. There are certain reasons for doubting this interpretation. The oscillatory behavior abruptly ceases after 350°C . without there being any significant change in the resistance of the sample. This eliminates the possibility of the crystal acting as a capacitor in the testing circuit, since the conductivity would be expected to increase abruptly when the crystal changes from a capacitor to a conductor. The resistance of the sample changes from $2.47 \times 10^{12} \Omega$ to $7.9 \times 10^{11} \Omega$ across the 50°C temperature change from 350°C to 400°C . This is not considered sufficient to change its properties to that of a conductor. Also, these oscillations disappear at a temperature which has associated with it the onset of an order-disorder transformation in the crystal. As will be seen in part B. of this section, a large number of vacancies are generated during the transition process. As previously discussed, these vacancies participate in strain release and supposedly in so doing eliminate the oscillations.

A way of picturing this process would be as follows. Suppose the charge carriers are electrons for the temperatures

below 350° C. It is not unreasonable to attribute impurity semi-conductor properties to the crystal at these temperatures. The strain condition of the lattice causes a change of the Fermi energy and in so doing allows electrons to go into the conduction band. The nonsymmetric amplitudes of the oscillations indicate that these electrons are released to the conduction band rather abruptly then slowly drop back into the valence band. This hypothetical model could function as follows. Under the strain condition, electrons are released from their "donor" atoms allowing the lattice to relax. As the electrons move away from their parent atoms, the strain condition begins to disappear and the electrons fall slowly back into the valence band with a resulting decrease in the conductivity. As the valence band fills, the lattice strain again builds up. When this lattice strain returns to a certain value, it will begin forcing electrons back into the conduction band. When the rate at which electrons are returned to the conduction band exceeds the rate at which they return to the valence band, the conductivity again increases. This causes the strain to relax again and the cycle continues. This process goes on until an equilibrium of some kind takes place. A general damping of the oscillations should be observable as this equilibrium between lattice relaxation and lattice strain is accomplished. Careful scrutiny of the oscillatory conductivity curves reveals the existence of such damping.

(B) Temperature in the range 400°C. to 500°C.

This interval is characterized by a monotonically increasing conductivity with time. This increasing conductivity is caused by the generation of charge carriers in the crystal. These charge carriers are ion vacancies formed by the disordering transition which commences near 400°C. It has been shown by Girifalco [1964] and Bushnev [1966] that one could expect an increased vacancy concentration in the disordered phase. These studies involve the theoretical determination of the equilibrium vacancy concentration in a simple two component crystal. Although microcline is much more complex than this, the general result for simpler systems should carry over. Girifalco shows that the vacancy concentration of a two component system will depend on the long range order parameter S in the following way:

$$n_v = \exp[-(E_v^0 + \frac{1}{4} Z v S^2)/KT]$$

S is the long range order parameter which is 1 at complete order and 0 at complete disorder. v is an ordering energy, E_v^0 a function of the ordering energy, and Z a numerical structure parameter.

This expression for the vacancy concentration is an equilibrium result. If the crystal is not at equilibrium in terms of S , then n_v will continually change as S changes. These

are conditions which control the conductivity curves of figures IV-5, IV-6, and IV-7. For these temperatures S decreases in time, and the conductivity increases in direct proportion to n_v .

(C). Temperatures above 500°C .

For temperatures above 500°C . the conductivity commences to decrease with time. This is probably a recombination process which depends on temperature and vacancy concentration. At sufficiently high temperatures, the ions will become mobile and recombine with the vacancies generated during the disordering process.

More detailed descriptions of the electronic and ionic mechanisms involved in the conduction process are difficult to give with any amount of certitude. This is because a complete knowledge of impurity content and structural transitions in this particular mineral are incomplete and perhaps even impossible to obtain. Any continued research on these conduction phenomena will have to be taken up on a crystal which is structurally simpler. If impurity content is to become a major issue, then naturally occurring minerals cannot be the subject of investigation.

VI. MODIFICATION OF ARGON FLUX BY AN ELECTRIC FIELD

A. Interpretation.

It has been found experimentally for temperatures above 400° C that the argon flux from the microcline feldspar can be increased by applying an electric field across the sample. The applied field must be of the order of a few hundred volts per centimeter in order to have an appreciable effect. The argon flux does not change monotonously with the applied electric field but rather goes through a series of maxima and minima as the field is increased.

There are several ways in which the argon flux could be increased with an electric field. The field could have a direct effect on the argon atom by physically moving a charged vacancy in which the atom is trapped. Since ionic current increases exponentially with field strength [Dekker, 1962, p. 177], the argon flux would increase exponentially with field strength. Modification in evolved oxygen flux showed a monotonic increase with electric field. This could be attributed to the fact that oxygen carries an intrinsic electric charge while contained in the lattice. Such a monotonic increase in the argon flux was not observed.

Attempts to explain the increase in argon flux by lattice distortions of piezoelectric origin encounter difficulties since the triclinic crystal system, to which microcline feldspar belongs, has a center of symmetry about each lattice point. [Berry and Mason, 1959, p. 29]. A necessary condition for the existence of piezoelectric properties is the lack of a center of symmetry in the class of symmetry to which the crystal belongs.

A mechanism which would explain both the increase in argon flux and the peaks in the modification of flux plots is a collision process. If the material contains a large enough number of mobile ions which are sufficiently massive to transfer energy to the argon upon collision, then all aspects of the phenomena could be explained. It is possible that a combination of collision and vacancy-atom movements are occurring together. There is a trend for the flux to increase in a continuous way with the maxima and minima peaks superimposed on this. The exponential trend could be due to the Maxwell-Boltzman distribution of argon atoms over their allowed energy states. The lower energy states would contain a proportionally greater number of atoms and these could be liberated with higher field collisions.

If a collision process is responsible for the increase in argon flux, it is necessary that there be a sufficient number of charge carriers available to do this. The following numerical calculation compares the increase in number of argon atoms coming from the crystal with the corresponding increase in current associated with the given change in voltage.

$$\Delta \text{Ar}^{40} = \frac{\Delta S}{R'} \frac{1}{1.6(10^{-19})} f = \frac{4 \times 10^{-2}}{1.6(10^{11})(10^{-19})} f$$

$$= 2.5 \times 10^6 \text{ atoms} \times f/\text{sec.}$$

$$\Delta K^+ = \frac{\Delta I}{1.6 \times 10^{-19}} = \frac{\Delta V}{R(1.6 \times 10^{-19})} = \frac{10^2}{(3 \times 10^9)(1.6)10^{-19}}$$

$$= 2.08 \times 10^{11} \text{ atoms/sec.}$$

ΔAr^{40} is the increase in the number of argon atoms observed at the collector of the mass spectrometer and f is (efficiency)⁻¹ of the mass spectrometer.

ΔS was the maximum change in the vibrating reed input voltage (40 mv).

R' is the input resistance of the vibrating reed electrometer (10^{11} ohms).

ΔK^+ is the increase in the number of ions participating in the conduction process.

ΔV is the change in applied voltage across the crystal.

R is the mean resistance of the sample at 450°C .

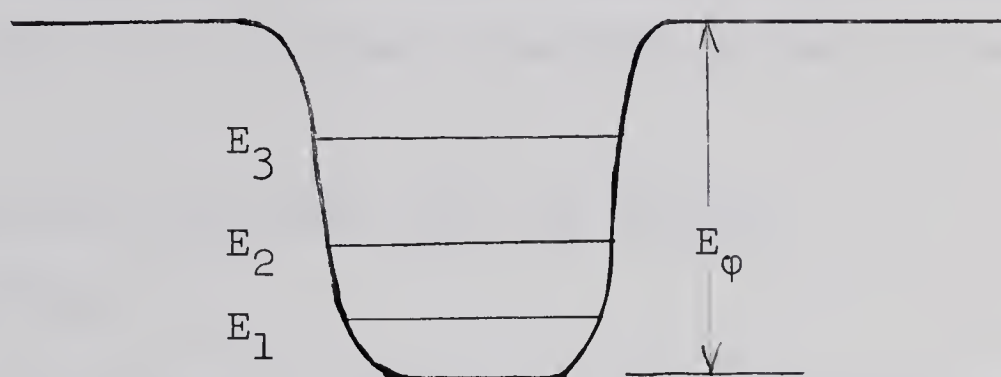
The value of " f " is typically of the order 10^3 .

Therefore this comparison shows ΔK^+ to be at least $10^3 \times \Delta \text{Ar}^{40}$.

In view of this, the increase in argon flux due to collision is reasonable, even when other contributions to the conduction process are considered.

The analysis of the collision phenomena will be deliberately kept as simple as possible in order that a preliminary interpretation can be made. Assume that all the incident ions are K^+ ions. (i.e. potassium ions). (It is possible for other ions to participate such as Na^+ , however we shall ignore their contribution for the moment.) According to the theory of ionic conduction, the maximum energy acquired by a charged ion will be determined by the distance over which it can be accelerated between potential wells. If the masses of the incident and target particle are equal (as is the case with K^{40} and Ar^{40}), a head-on collision could result in complete energy transfer from incident to target particle. For the sake of simplicity we shall assume this to be the case in the present analysis. A more detailed account of the scattering process can be used in experiments where better control is available. This exchange of energy should manifest itself as a change in the activation energy of diffusion for the argon

atoms. Energy transferred to the argon atoms can be interpreted as contributing to the redistribution of these atoms over the energy states available to them in their potential wells. The following diagram illustrates a hypothetical energy level scheme for a trapped atom and defines the activation energy.



The measured value of the activation energy E_ϕ is the height of the potential barrier above the ground state of the argon atom. If the energy of the incident ion matches the difference in energy between two successive states available to the argon atom, it will transfer this energy in such a way as to elevate the argon atom to the next higher energy level. Collisions which do not meet these requirements, will not result in energy transfer. Ions which constitute the electric current, will have a distribution in energy due to thermal

velocities. This introduces a spread in the electric field values corresponding to maximum energy transfer to the argon atom. Therefore, a statistical uncertainty arises in the determination of the maximum energy transfer at resonance.

As the accelerating voltage is increased, the collisions will result in a redistribution of the argon atoms over the energy states available to it. The higher levels will be more populated than under thermal equilibrium and the net result will be an apparent lowering of the activation energy.

(B) Information Obtainable from the Effect.

(1) Energy States

The change in argon flux can be used to get estimates of the energy transferred to the argon atom and from this a knowledge of the separation of energy levels for the trapped argon atom. These states will be determined by the shape of the potential well in which the argon is trapped.

The theory of diffusion requires that $F = -D \frac{dc}{dx}$. F is the flux, D the diffusion coefficient, and $\frac{dc}{dx}$ the concentration gradient. A change in flux will appear as a change in the mass spectrometer output signal. If the collisions do not appreciably modify the concentration gradient, the following method could be used to determine the energy transferred to the argon atom.

Since $F = -D \frac{dc}{dx}$

then

$$\ln |F| = \ln D + \ln \frac{dc}{dx}$$

but

$$D = D_o e^{-E_\phi/KT}$$

so

$$\ln |F| = \ln D_o - \frac{E_\phi}{KT} + \ln \frac{dc}{dx}$$

$$\delta \ln |F| = \delta \ln D_o - \frac{\delta E_\phi}{KT} + \delta \ln \frac{dc}{dx} \quad .$$

If it is assumed that the collisions do not affect D or the concentration gradient $(\frac{dc}{dx})$, then the change in these quantities due to collision will be zero.

Therefore,

$$\delta \ln |F| = - \frac{\delta E_\phi}{KT} \quad \text{VI-I}$$

Let $\alpha \mathcal{E}$ be the energy acquired by an ion due to its acceleration by the electric field. Then $\delta E_\phi = (\alpha \mathcal{E})$ for a direct collision with total energy transfer.

When making a series of measurements, $\mathcal{E}$ is continually incremented from 0 to 5×10^4 volts/cm. In this case there will be a change in $\delta \ln F$ caused by a change in field $\Delta \mathcal{E}$.

Therefore
$$\frac{\Delta(\delta \ln F)}{\Delta E} = - \frac{\alpha}{KT} \quad \text{VI-II}$$

It was found that the results were more clearly detectable if the analyses were done in this way.

The quantity α is a coupling factor which will be equal to the mean free path of the incident ion at maximum energy transfer. The experimental results of applying equation VI-II to the data obtained on the increased flux due to electric field are presented in Figure VI-1 and VI-2. A clear quantum effect is observable and tentative interpretations may be proposed.

Since the argon atom is considered to be electrostatically neutral and spherically symmetric, a three-dimensional square-well potential may be used to mathematically describe its interaction with the trapping site. (The shape of the well will actually be controlled by crystal symmetry). An elementary quantum description for this system is given in Schiff [1955, p. 76]. Figure VI-2 shows a comparison of the experimental spectra for various temperatures with the theoretical spectra for an argon atom in a three dimensional square well. The theoretical spectrum labelled A was calculated using a 2 angstrom well radius and an accelerating distance or mean free path of 5 angstroms. An identical

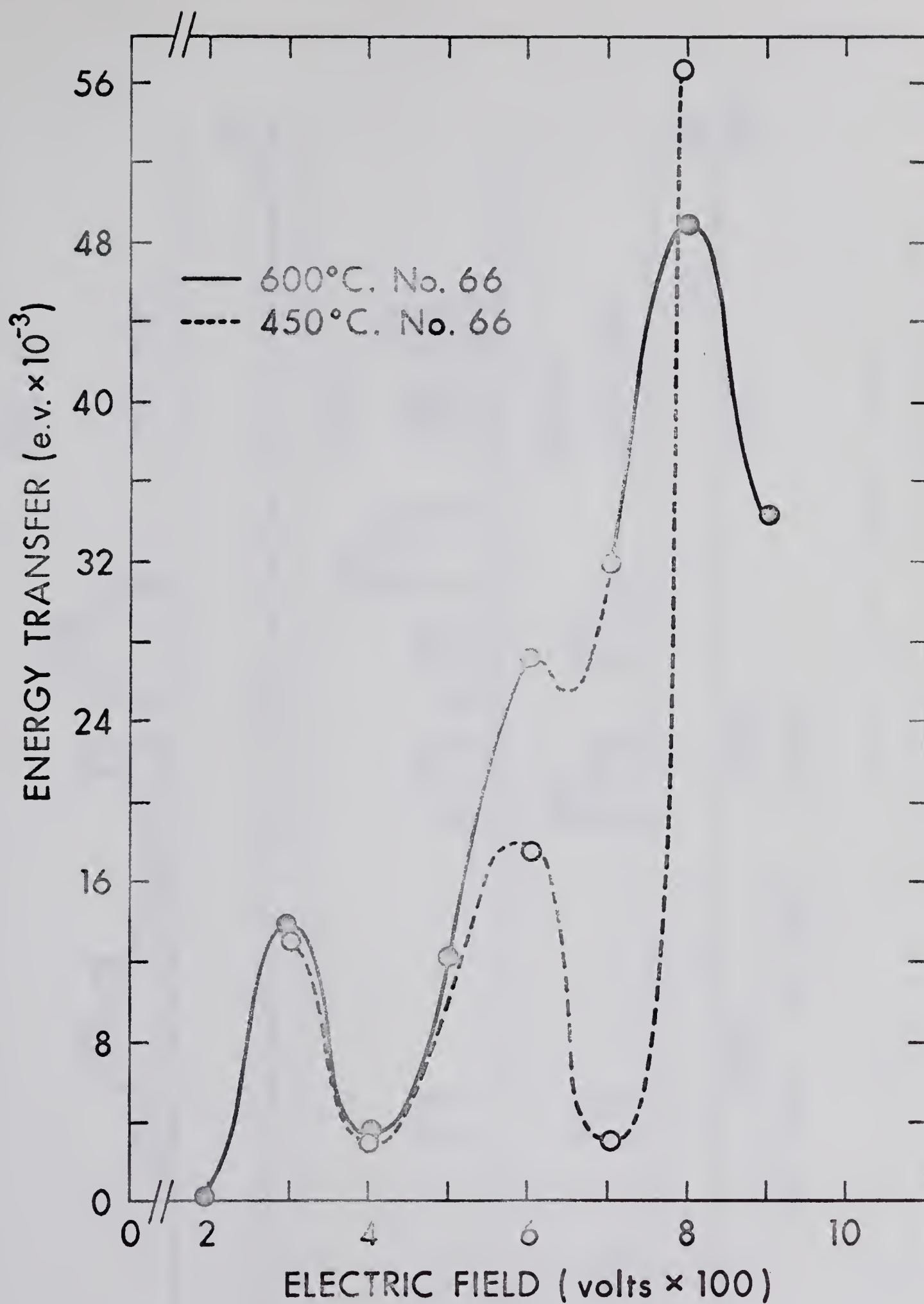


Figure VI-1 Energy Transferred to Argon Atom as
a Function of Applied Electric Field.

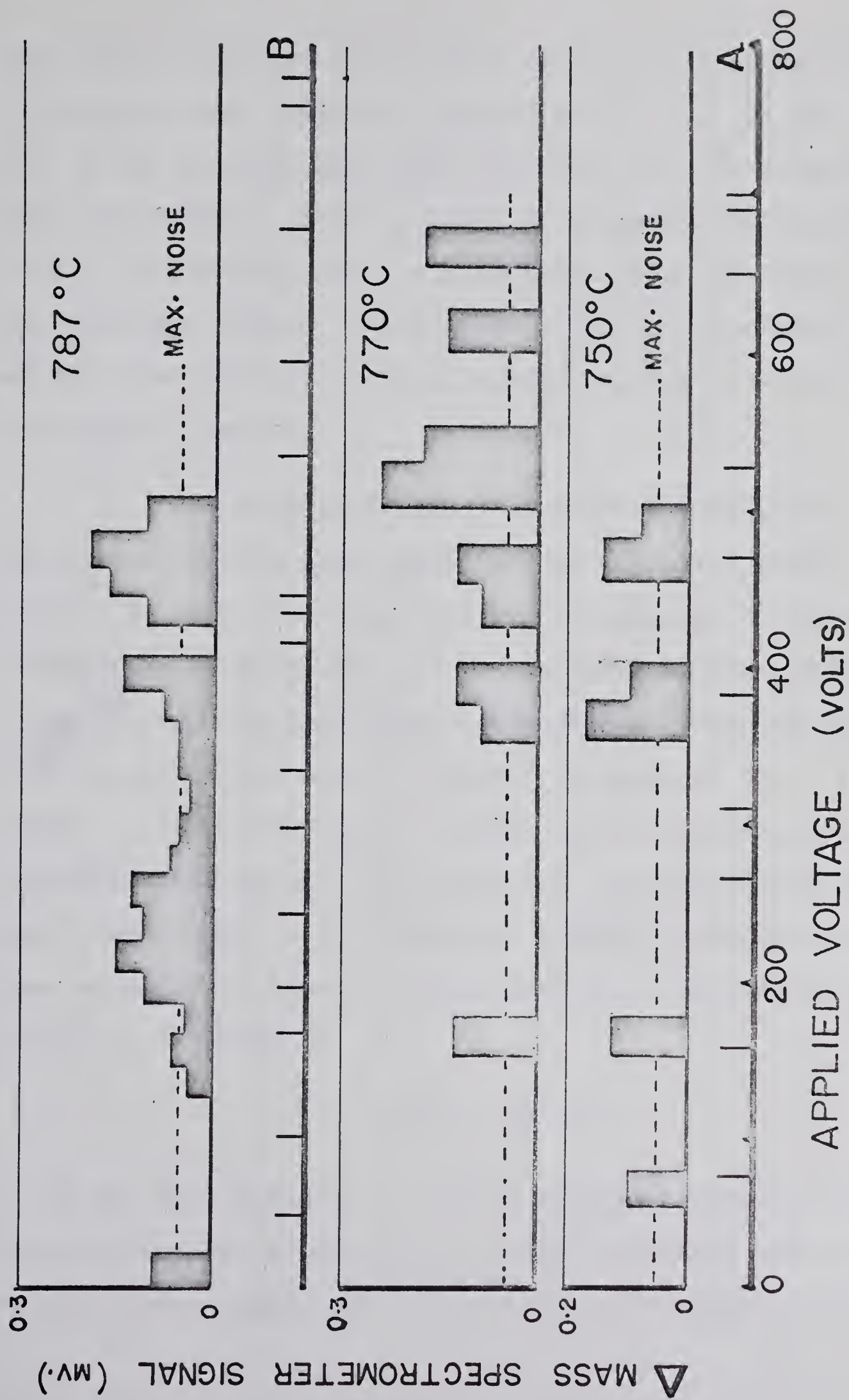
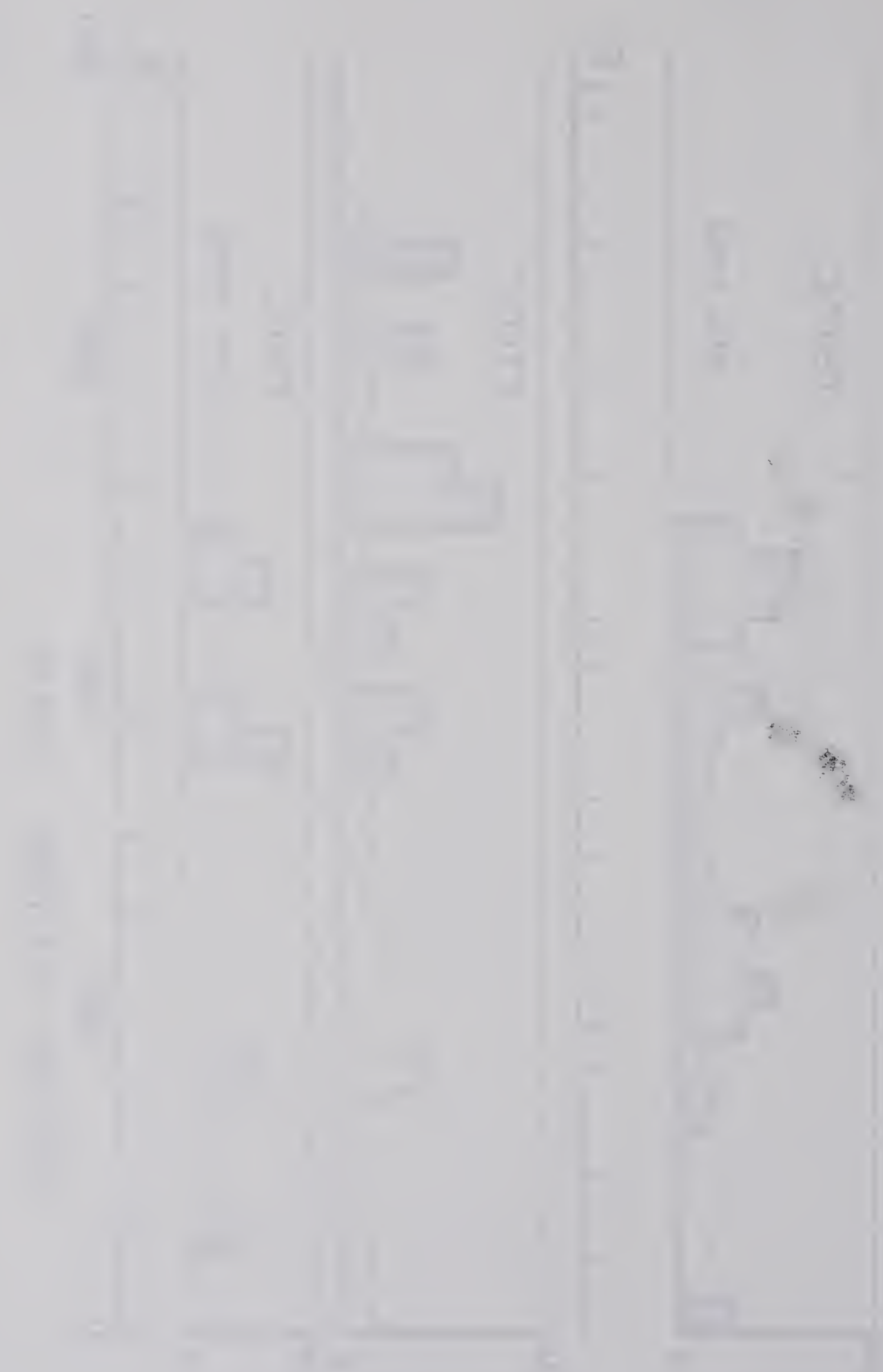


Figure VI-2 COLLISIONAL SPECTRA (Change in Argon Flux vs. Applied Field)



Graph showing the relationship between time and distance for an object moving at a constant speed.

spectrum is obtained if the well radius were increased to $4 \text{ \AA}$ and the mean free path reduced to $1.25 \text{ \AA}$. If the well width is $4 \text{ \AA}$ and the mean free path increased to $2 \text{ \AA}$, a more compact spectrum results. This is labelled as spectrum B in the figure. It will be noticed that the high temperature spectrum is qualitatively similar to spectrum B (due to increased dimensions) whereas the lower temperature spectra appear to be more like theoretical spectrum A.

The classical theory of diffusion requires that the diffusing atom make jumps between potential wells. While an atom is in a potential well, it is assigned a certain "vibrational" frequency ν . For a comprehensive discussion of this, see Vineyard [1957]. The rate at which an atom jumps from one potential well to another is given by $w = \nu e^{-E/KT}$ where ν is the effective vibrational frequency and E is the activation energy. The observed "inverse square root of mass" dependence for diffusion of different isotopes of the same material is based on this equation. The diffusion coefficient D is given as

$$D = P \nu a^2 f$$

a is the jump distance, f is a correlation factor which takes into account the tendency for an atom to make a certain number of non-random jumps, and P is a fraction close to unity.

If a quantum picture is used for describing diffusion, then the probability of the atom jumping to another potential well will be determined by the energy state it is in, since this controls the probability for the atom being in the energetically forbidden region between wells. An accurate determination of the energy states for the trapped atom will allow for the construction of its wave functions and a theoretical determination of the diffusion coefficient on quantum principles. This will require a highly accurate spectrum for the bound states. The present study does not concern itself with this particular problem but rather uses additional information concerning the mean lifetime in these states to resolve the problem of argon diffusion in feldspar.

This is taken up in part 2 of this section.

(2) Relaxation of Collision Excitation

If the increase in argon flux caused by ion-atom collisions is allowed to stabilize and afterwards the electric field turned off, a decay of this flux will commence. This decay is due to atoms in excited states dropping back to lower energy levels. This de-excitation could be from higher bound states or from energies which are above the potential of the trapping sites. The latter case requires that the atom be retrapped before undergoing de-excitation.

Prior to turning on the electric field and modifying the argon flux, one first obtains a stable thermal diffusion flux. If sufficient time has passed, the exponential tail of the diffusion curve will be under observation and will represent a nearly constant flux during the time of the collisional experiments. When an electric field is applied, this "thermal flux" is modified by the addition of a "collisional flux." The collisional flux is generated by reducing the activation energy of argon atoms through excitation to higher levels in the potential well. The collisional relaxation times are the rates at which these atoms return to lower levels when the electric field is removed.

The total flux is given by

$$F_{\text{(total)}} = F_{\text{(thermal)}} + F_{\text{(collisional)}}$$

At equilibrium there are a certain net number of argon atoms in the first excited state. In this case

$$|F_T| - |F_{th}| = |F_{coll}| = {}^1D \frac{\partial C_1}{\partial x}$$

where 1D is the diffusion coefficient for diffusion out of the first excited state. C_1 is the volume concentration of atoms in the first excited state.

$$C_1 = N_1 g(x)$$

where $g(x)$ is the initial spatial distribution of diffusing substance. The collisional flux is then given by

$$|F_T| - |F_{th}| = {}^1DN_1 \frac{\partial g(x)}{\partial x}$$

The number of atoms in the first excited state will decrease with time after the electric field is turned off. This time dependence will be given by

$$N_1 = {}^1N_0 e^{-\beta_1 t}$$

1N_0 is the number in state 1 at $t = 0$ (i.e. when field is turned off.) and β_1 is the transition probability per unit time. The mean life of an atom in this state will be given by

$$\frac{1}{\beta_1} = \tau_1$$

The time dependence of the collisional flux becomes

$$F_{\text{coll}} = F_{\text{total}} - F_{\text{thermal}} = {}^1\text{D}^1\text{N}_0 \frac{\partial g(x)}{\partial x} e^{-\beta_1 t}$$

VI-3

$$\text{Ln} (F_t - F_{\text{th}}) = \text{Ln} {}^1\text{D}^1\text{N}_0 \frac{\partial g(x)}{\partial x} - \beta_1 t$$

This is the equation used to calculate collisional relaxation times. The logarithm of the collisional flux versus time should be a straight line with a slope given by the transition probability per unit time.

Figure VI-3 shows the results for the temperatures 450° C, 500° C and 600° C. It will be observed that there are two straight lines in this relaxation. This may be interpreted as de-excitation from two different levels, and the slopes of each line give the transition probability per unit time from each level. The reciprocal of this slope is the mean life and represents the average time that an atom remains in its excited state. These values range from approximately 6 minutes to 1 hour and are anomalously long for mean life-times. This can indicate that either the model chosen is incorrect, or else the de-excitation coupling of the argon atom with the crystal lattice is very poor.

One possibility for this latter interpretation can be that the square well states which the argon atom should possess are not spaced in a way which allows for absorption of quanta from a harmonic type field which the lattice represents. If this were the case, the transitions would be forbidden and the mean lifetimes very large. More comprehensive energy spectrums and relaxation data along with theoretical calculations of quantum transition probabilities will be required in order to resolve this issue.

The above discussion attempted to explain the increase of the relaxation times in terms of quantum transitions between bound states. An alternative explanation could be made in terms of increasing diffusion trapping lengths with time. This would occur if the relaxation effect represented a classical retrapping. The number of available trapping sites would decrease with time (due to their being filled) and the distance an argon atom must travel to be trapped would therefore increase, causing an increase in the relaxation time.

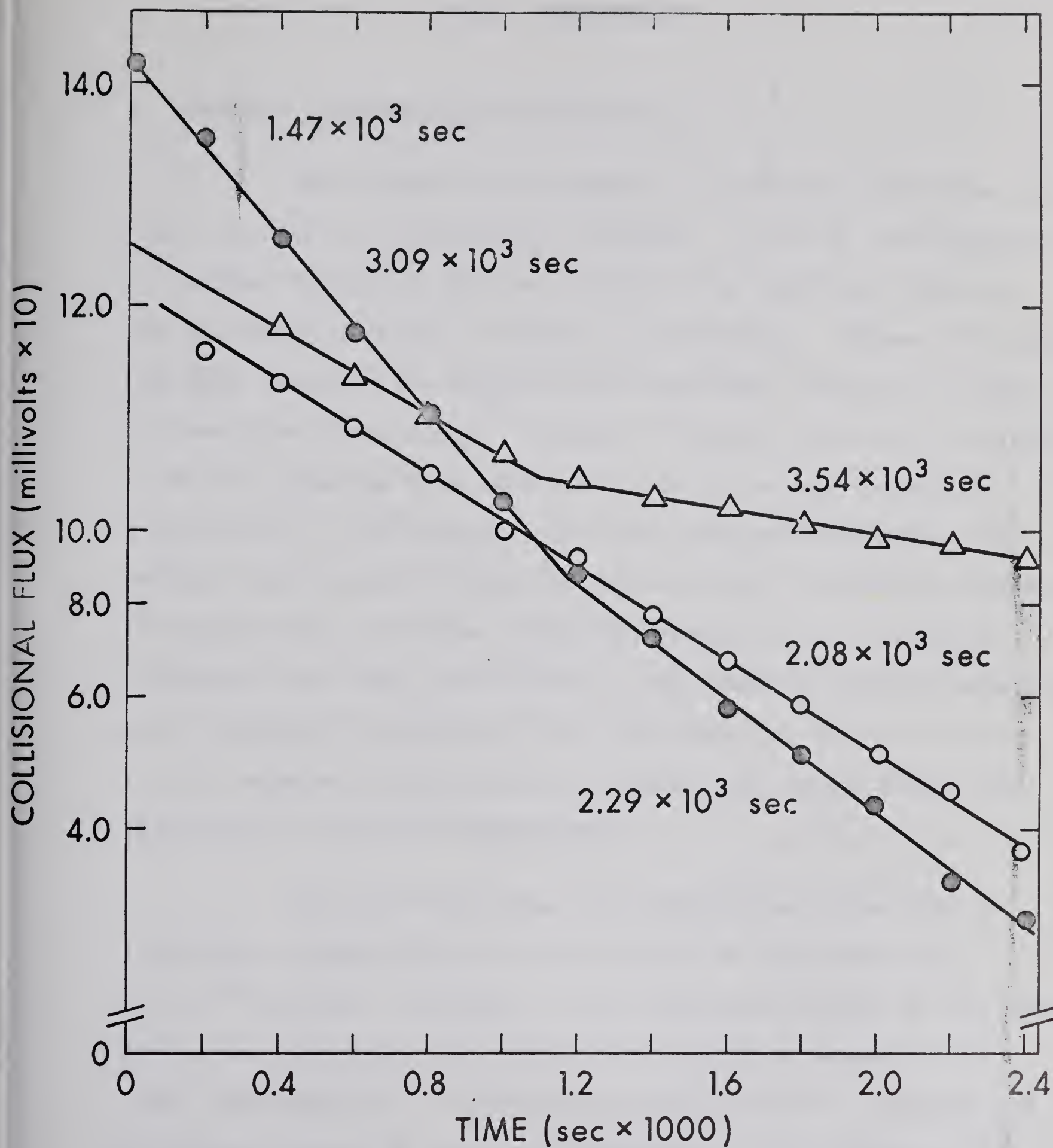


Figure VI-3. Relaxation of Collisional Flux.

VII. DISCUSSION

A. General Consideration of Results.

This thesis has attempted to study the mechanism of argon diffusion in microcline feldspar. It is an investigation of thermal diffusion and the effects of an electric field on the diffusion behavior of argon in microcline. Thermal diffusion has been followed by observing the flux-time behavior of argon evolved from the crystal. A model of simple diffusion according to Fick's laws has been used and found to be only partially satisfactory. The overall flux-time relationships appear to deviate from perfect Fick's law behavior due to other processes. The possibility of these deviations being due to a trapping phenomenon has been investigated. The trapping process appears as an anomalous lowering of the flux from its expected value. It also appears in the form of a larger activation energy for diffusion at elevated temperatures.

The flux-time data for temperatures below 500° C indicates a large diffusion coefficient of the order of $5 \times 10^{-8} \text{ cm}^2/\text{sec}$. Likewise, a low activation energy of the order of 0.1 e.v. is found for the binding energy of argon at the lower temperatures. A transition occurs at 450° C accompanied by several orders of magnitude decrease in the diffusion coefficient. The electrical conductivity data imply that a

high degree of disordering takes place over the transition temperature interval of 400°C to 500°C . The disordered state is observed in the form of a time dependent increase in the number of charge carriers. Since microcline is an ionic conductor [Amirkhanoff, 1961], it implies that these charge carriers are point defects involving interstitial ions and vacancies. After the transition, these point defects appear to decrease with time. The activation energy for argon diffusion becomes much larger ($\sim 35\text{ K Cal/mole}$ or $\sim 1.5\text{ e.v.}$) immediately following the transition. This high activation energy could indicate that the argon atoms have become trapped since normal lattice binding energies for a neutral argon atom would never exceed a fraction of an electron volt.

A theoretical estimate for the activation energy of argon diffusion may be obtained by calculating the binding energy of an argon atom in a typical lattice position of feldspar. Because of its electrical neutrality, the attractive forces on an argon atom will be of Van der Waals origin only. The potential of an attractive Van der Waals force may be written as [Wanier, 1959]

$$u = - \frac{3}{2} \frac{I_1 I_2 \alpha_1 \alpha_2}{I_1 + I_2} \frac{1}{R^6} \quad .$$

I_1 and I_2 are the ionization potentials for the atoms undergoing the attraction. α_1 and α_2 are the respective electronic polarizabilities. R is the separation distance of the two atoms.

The dominant term in the binding energy is the equilibrium separation R since it appears in the equation as a reciprocal sixth power. The equilibrium separations of a normal potassium lattice site in feldspar is such that there are $\sim$ eight bonds between it and the nearest neighbors. The potassium atom is supposedly coupled to 8 oxygen atoms. Since argon is formed by nuclear transmutation of potassium, a first approximation to the argon lattice position is a potassium site. The mean center-to-center distance between a potassium ion and the atoms surrounding it is $\sim 3 \text{ \AA}$. The fact that Van der Waals binding drops off as $1/R^6$ means that only nearest neighbors will make a significant contribution to the binding energy.

The values for ionization potentials of various ions may be obtained from Kleinberg, Argersinger and Griswold [1960, p. 96]. The polarizabilities are obtained from Pauling [1927, pp. 191 and 198]. This information is listed in the following table.

Data Required for Calculating Van der Waal's Binding Energy

Element	Ionization Potential (e.v.)	Polarizability (cm ³)
Ar	15.76	1.625×10^{-24}
O ⁻²	2.2 (elec. AFF.)	3.90×10^{-24}
Al ⁺³	119.96	5.38×10^{-26}
Si ⁺⁴	166.73	3.32×10^{-26}
K ⁺¹	31.81	8.40×10^{-25}

The attractive potential between an oxygen ion and argon atom separated by 3 Å is $U_{O^{2-}-Ar} = .0253$ e.v. The equilibrium configuration of an argon atom in a potassium site is such that 8 oxygen bonds are experienced. The total attractive potential due to its interaction with nearest neighbor oxygen is $8 U_{O^{2-}-Ar} = 0.192$ e.v. If second nearest neighbors are considered, one has approximately 6 silicon atoms and 2 aluminum atoms at ~ 5 Å. Van der Waals attraction becomes negligible at this range compared to nearest neighbor forces. The attractive potential between a Si atom and an Ar atom at 5 Å is $U_{Si^{++}-Ar} = 7.32 \times 10^{-7}$ e.v. The potential due to Al⁺³ will be similar to this. Eight such bonds give a total energy of 5.89×10^{-6} e.v. which is negligible compared to the attractive potential due to nearest neighbor forces.

Thus, the total binding energy of an argon atom is calculated to be 0.192 e.v. or 4.42 K Cal/mole. This

should represent a first approximation to the activation energy of diffusion for argon in microcline. Gentner et al [1960] have observed activation energies of this order for argon diffusion in potassium-bearing minerals between the temperatures 100°C to 450°C , however experimental values from microcline for temperatures below 500°C are approximately one half the predicted value. For temperatures above 500°C , it is many times greater than this. Activation energies of the order of 1.5 e.v. were found for temperatures above 500°C . This large activation energy at elevated temperatures is found by other workers also [Amirkhanoff, 1961; Baadsgaard et al, 1961; Newland, 1963]. As pointed out by Sardarov [1961], these activation energies at high temperature probably represent the rupture of ionic bonds which release argon atoms from trapping sites. The activation energy for temperatures below 500°C is considerably lower than the calculated value and suggests that the atomic diffusion of argon at these temperatures does not take place by the movement of argon from one potassium site to the next. The low activation energy indicates that the argon atom is activated out of regions of considerably larger volume than that afforded by a normal K site. There are two immediate possibilities which could explain this effect. The first is that argon, with a radius slightly larger than the K^{+} atom, will not be readily accommodated in the K^{+} lattice

site. The argon atom also receives 30 e.v. recoil energy upon its creation from potassium. Normal energies required for the creation of Frenkel defects are of the order of 1.5 e.v. to 2.0 e.v. Thus, one can reasonably suspect that the argon atom will be driven into a region more compatible with its size. Reference to the photographs of the feldspar lattice model in figure 2 of the introduction reveals that these regions of larger volume could be the channels along the b- and c- axes. Once an argon atom gets into these, it will tend to stay there and migrate along the channel axis which represents a path of least resistance. As long as the lattice remains reasonably rigid and intact, there will be no reason for the argon atoms to deviate from motion along these channels. However, once a large amount of defects and dislocations are introduced, the perfect lattice structure becomes modified, and the continual movement of argon along these channels is impeded. The argon atoms will then begin interacting with the vacancies and dislocations in a way which completely changes the diffusion characteristics.

A second possible explanation for the low temperature diffusion is a model of grain boundary and dislocation diffusion patterned after that of Fisher [1951]. This model could be used to explain channel diffusion and diffusion along dislocations. It does not explain diffusion on an atomic

scale as the previous model attempts to do, but rather discusses the diffusion rate in terms of high diffusivity pathways which penetrate the crystal. Some of the salient characteristics of the low temperature flux-time data (Figures IV-1 to IV-6) are in keeping with this model. One characteristic is that the large diffusion coefficient which presumably exists for the low temperatures, is associated with only a small fraction (less than 10%) of the argon which could be released from the sample [Baadsgaard et al, 1961]. Diffusion along dislocations would give this result since, a high diffusion coefficient will be in effect along the dislocation but a small reservoir of gas will be associated with it. The numerical calculations of Fisher indicate that initially there will be a large flux of diffusing material (along the dislocation line) which rapidly decreases to nearly a steady state value. The final value is controlled by the rate at which gas is supplied to the dislocation line from the lattice. Newland [1963] also observed a high initial flux rate for the low temperature diffusion of argon in microcline; however, he chose to analyze only the final steady state flux in his calculation of the diffusion coefficient. He considered this to be more representative of the lattice diffusion.

The flux-time equations which have been used in the present study have not included those which describe grain boundary or dislocation diffusion. If dislocation diffusion is in effect and the dislocations are numerous and randomly oriented, the equations of Chapter III should explain the flux-time curves since an average effect would be observed. The only parameter which would be affected is the sample dimension ℓ . Diffusion from multiply-misoriented grains would require the use of a term $\langle \ell \rangle$ in place of the wafer thickness, where $\langle \ell \rangle$ is the mean linear dimension of the grain or material enclosed by dislocations. Intuitively, one would expect that a high density of multiple dislocations should not affect the shape of a normal flux-time equation. Levine and MacCallum [1959] have shown that this is not the case. Their analysis of diffusion in polycrystalline materials suggests that results similar to those of Fisher should be obtained. Another reason for expecting an observable effect peculiar to dislocation diffusion is the unique characteristic in microcline of having regularly spaced repeated twinning. This results in a regular spacing of parallel dislocations. Likewise, there is a regular intersection of twin planes which develop a series of dislocation lines all oriented in the same direction. It is observed that this twinning does not disappear at the first transition near 450° C. Therefore, if

diffusion along twin dislocations is observable, it should persist to temperatures above 500°C , provided the necessary conditions for the observation of grain boundary diffusion exist. These conditions are outlined by Levine and MacCallum [1959] and reviewed by Shewmon [1963]. The principle condition for the observation of dislocation diffusion is that $D_{\text{lattice}}/D_{\text{dislocation}}$ be less than $\sim 10^{-5}$. Since the dislocation lines in microcline will be regularly spaced and parallel, it may be possible to simply average Fisher's result for a single dislocation over the distance between dislocations. A model such as this requires significantly different flux-time equations from those used in Chapter III. It is hoped that the form of the flux-time curve will be sufficiently definitive to decide between the models of Chapter III and dislocation diffusion. A thorough examination of the flux-time data will be conducted in the future to determine whether such a distinction can be made.

B. Retention of Radiogenic Argon in the Feldspar System.

It has been found that argon diffusion in microcline feldspar does not obey simple diffusion laws and a concept of atomic trapping has been introduced to explain the experimental results. This trapping is thought to be associated with single vacancies or vacancy clusters which are initially present as Frenkel defects in equilibrium with the lattice or as defects generated by phase transitions.

The effect of transitions on the diffusion data may be detected by plotting logarithm of argon flux (at a particular time on the diffusion curve) against reciprocal temperature. Best results are obtained if the time on the diffusion curve is chosen near the point representing maximum argon flux (i.e., maximum output voltage of the mass spectrometer). A plot of $\ln V_{\max}$ versus reciprocal temperature will be controlled by E_{ϕ} , the activation energy, and D_0 , the pre-exponential factor in the Arrhenius equation for the diffusion coefficient. The functional relationship for $\ln V_{\max}$ vs. $1/T$ as given by equation III-22 is:

$$\ln V_{\max} = \frac{E_{\phi}}{KT} - \frac{\ell^2}{D_0 \pi^2 \tau} \exp [E_{\phi}/KT] + \frac{2.3 C_0}{D_0} \left(\ell^{\frac{3}{2}} / 4 \tau \pi^{\frac{3}{2}} \Omega^{\frac{1}{2}} \right)^2$$

Equation III-6 gives the following expression for $\text{Ln } V_{\text{max}}$ vs. $1/T$:

$$\text{Ln } V_{\text{max}} = \frac{1}{2} \text{Ln } D_0 - \frac{E_{\phi}}{2KT} + \text{Ln } \frac{A \Omega}{t^{1/2}}$$

E_{ϕ} activation energy

τ time

K Boltzman's Constant

D_0 pre-exponential factor

T absolute temperature

Ω constant

l thickness of sample

(D_0 is defined through the equation $D = D_0 \exp [-E_{\phi}/KT]$ where D is the diffusion coefficient).

These functions have no discontinuities for the physically possible values of the parameters. Thus, any discontinuities which appear in the experimentally determined curve will be due to abrupt changes in E_{ϕ} and D_0 . These changes will be caused by modifications in the diffusion coefficient resulting from structural transitions. For the benefit of the reader, Figure IV-A is repeated here as Figure VII-1. The plot of $\text{Ln } V_{\text{max}}$ versus $1/T$ shows a major change in the diffusion parameters between 450°C and 500°C . This is supported by a change in the activation energy for ionic conductivity. This change is initiated by a discontinuity in the Arrhenius plot for conductivity [Lipson and Pronko, 1962].

A second break is seen to occur between 600° C and 650° C. The inset of Figure VII-1 is a specific heat plot taken from Amirkhanoff [1961]. It may be observed from this that the transition is a slow one, occurring over a span of several hundred degrees. Amirkhanoff classifies this as a second order transition. Transitions of the second order are usually associated with disordering phenomena; however, their characteristic specific heat plots are not like the published curve of Amirkhanoff [1961].

The conductivity data in Figures IV-5 to IV-7 indicate that a large concentration of vacancies are being generated in the interval 400° C to 500° C. It has been reported by Spencer [1937] that microcline samples, which he studied, showed a decrease in specific gravity and refractive index with temperature starting at $\sim 400^{\circ}$ C. Rosenholtz and Smith [1942] showed that microcline exhibited measurable discontinuities in volume beginning near 400° C. These effects are consistent with the large generation of vacancies exhibited by an increasing conductivity with time. Girifaleo [1964] has shown theoretically that the number of vacancies in a crystal will increase upon disordering in a way that is proportional to the negative exponential of the long range order parameter. Buerger [1948] has discussed the role of Si-Al disordering in feldspars and considers the effect of

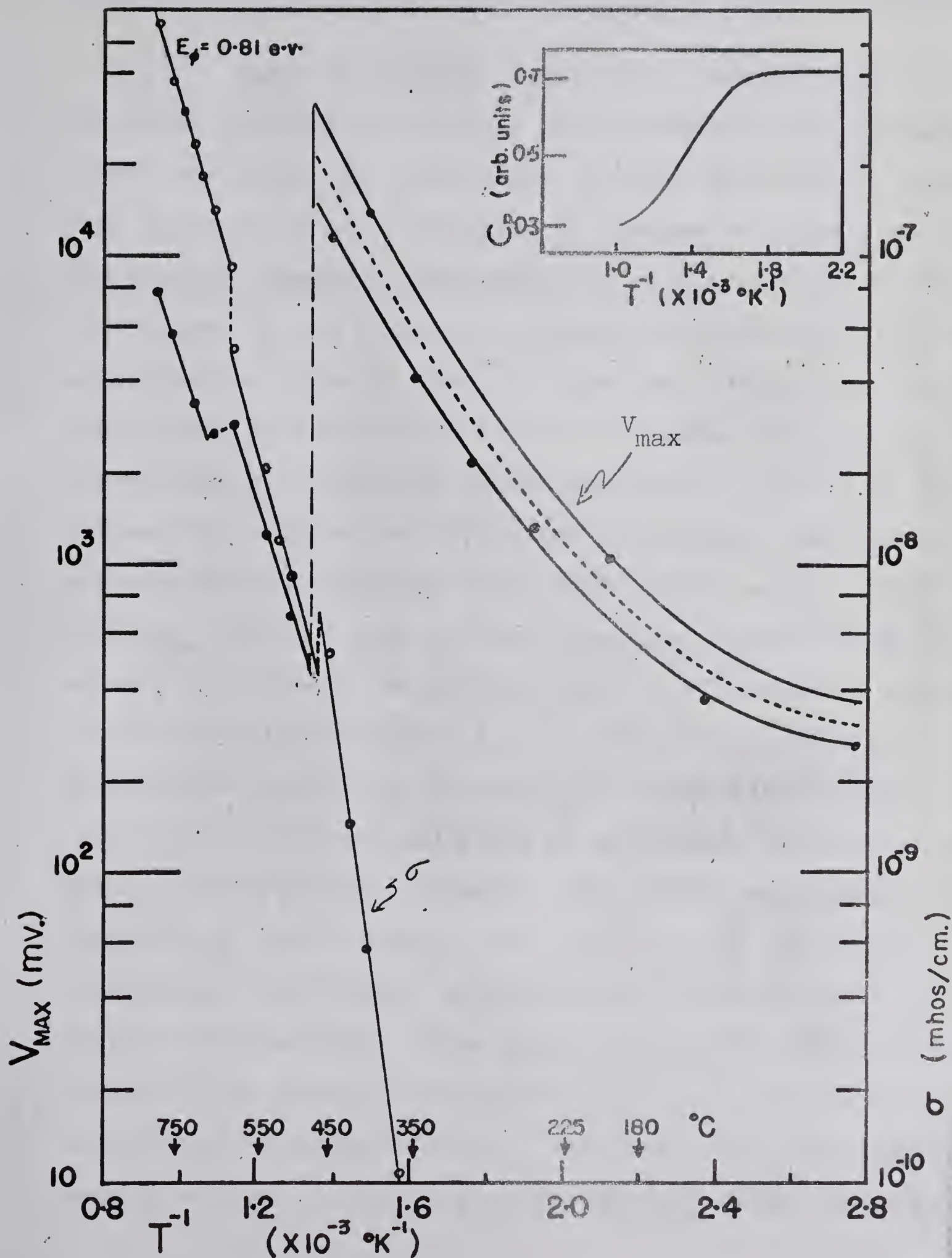


Figure VII-1. $\ln V_{\text{max}}$ and $\ln$ Conductivity versus $1/T$.

Inset: Specific Heat Data from Amirkhanoff [1961].

temperature on the redistribution of these atoms in microcline.

Baily and Taylor [1955] did a careful study of a triclinic microcline structure and presented several important ideas concerning the observation of Si-Al disorder in feldspars. They point out that in addition to changes in refractive index and specific gravity, order-disorder relationships can often be detected by the presence or absence of super-structure or super-lattice lines in the X-ray spectra. These lines are not present in the ordered forms of feldspar although the differences in refractive index and specific gravity do exist between the ordered and disordered polymorphs. They go on to explain that superlattice X-ray reflections (which indicate ordering) are not to be expected from the ordered feldspars owing to the similar scattering power of aluminum and silicon and the low Al:Si ratio of 1 to 3. They point out that plagioclase ($\text{NaAlSi}_3\text{O}_8$) is similar to microcline in its Al:Si ratio of 1 to 3 and there is an absence of superlattice reflections here also. However, the crystal anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) with a larger Si:Al ratio of 2:2 does show superlattice reflections and a doubled c-axis relative to albite and microcline. Thus Baily and Taylor [1955] conclude, "Proof of the nature of the distribution of aluminum and silicon can be provided only by detailed atomic structure determinations. Although electron density values alone will

not distinguish the two atoms (i.e., Si and Al) because of similarity in atomic number, aluminum is slightly larger than silicon so that precise interatomic distance measurements should differentiate them"

In contrast to this problem, one would expect a sharp change in the X-ray pattern when perthitic homogenization occurs due to the large size difference between K and Na.

Goldsmith and Laues [1954] have carried out X-ray experiments on a variety of microcline samples by heating them at various temperatures for given intervals of time and then observing the X-ray powder diffraction. They base their decision concerning the relative triclinicity of a lattice on the spacing between the (131) and ($1\bar{3}1$) lines. Their justification for this is the fact that a number of reflections from a monoclinic structure are split into doublets with significant separation as compared to triclinic polymorphs of the same material. It would seem, in the light of Baily and Taylor's comments, that such an effect should not occur from the simple disordering of Si and Al. However, it is the opinion of Baily and Taylor that the Si:Al order/disorder controls the structure of the unit cell. (Triclinic for the ordered system and monoclinic for the disordered system). A difference in crystal symmetry should be observable on a

diffraction pattern and this is the criterion on which Goldsmith and Laues [1954] based their conclusions. Goldsmith and Laues [1954] were not able to detect any change in the crystal structure of microcline by heating it for several hundred hours in the temperature range near 550°C ; however, if the crystal were heated under $8,000\text{ lbs/in}^2$ of water pressure at these temperatures, a detectable change in crystal structure occurred. These authors were able to demonstrate that the material which had changed its crystal symmetry was only the surface layer while the interior remained unchanged. They concluded that part of the surface material goes into solution and reprecipitates in the new monoclinic crystal symmetry. They emphasize that this is not simply a lattice transformation of microcline to sanidine in the one component system KAlSi_3O_8 .

If it is postulated that a certain amount of Si-Al disorder can take place without an observable change in the crystal symmetry, and if the transformation temperatures from the present work (and the work of Spencer [1937] and Rosenholtz and Smith [1942]) is compared to the phase diagram of Smith [1960], an immediate correlation of the transport properties in microcline with the percent Si-Al order in this mineral is observed.

Figure VII-2 is a diagrammatic description of the processes associated with the disordering. These include the qualitative changes observed in the measurements of argon diffusion and electrical conductivity as the various stages of possible disorder are encountered. A very important distinction must be made between the nature of the observed disorder in these crystals (as described by Smith [1960] and other workers), and the way in which these concepts are applied to microcline in the present work. Currently established theories on the delineation between sanidine, orthoclase, and microcline are based on the relative ordering between Si and Al atoms in the structure of feldspar. Sanidine is a highly disordered form of microcline and is generally crystallized under conditions of rapid cooling. Microcline is considered to have formed under conditions of slow cooling and after crystallizing in an ordered state, it is thought to convert from an initial monoclinic form (as characterized by sanidine and orthoclase) to a triclinic form by a process of multiple body twinning [Berry and Mason, 1959]. It is in this heavily twinned triclinic form that microcline is found in nature. The conversion of microcline to its triclinic form by multiple body twinning is an alternative to the theory that its triclinic form is caused by Al-Si disorder. Orthoclase exists in a monoclinic form and has an ordering which is somewhere between microcline and sanidine. It appears that a

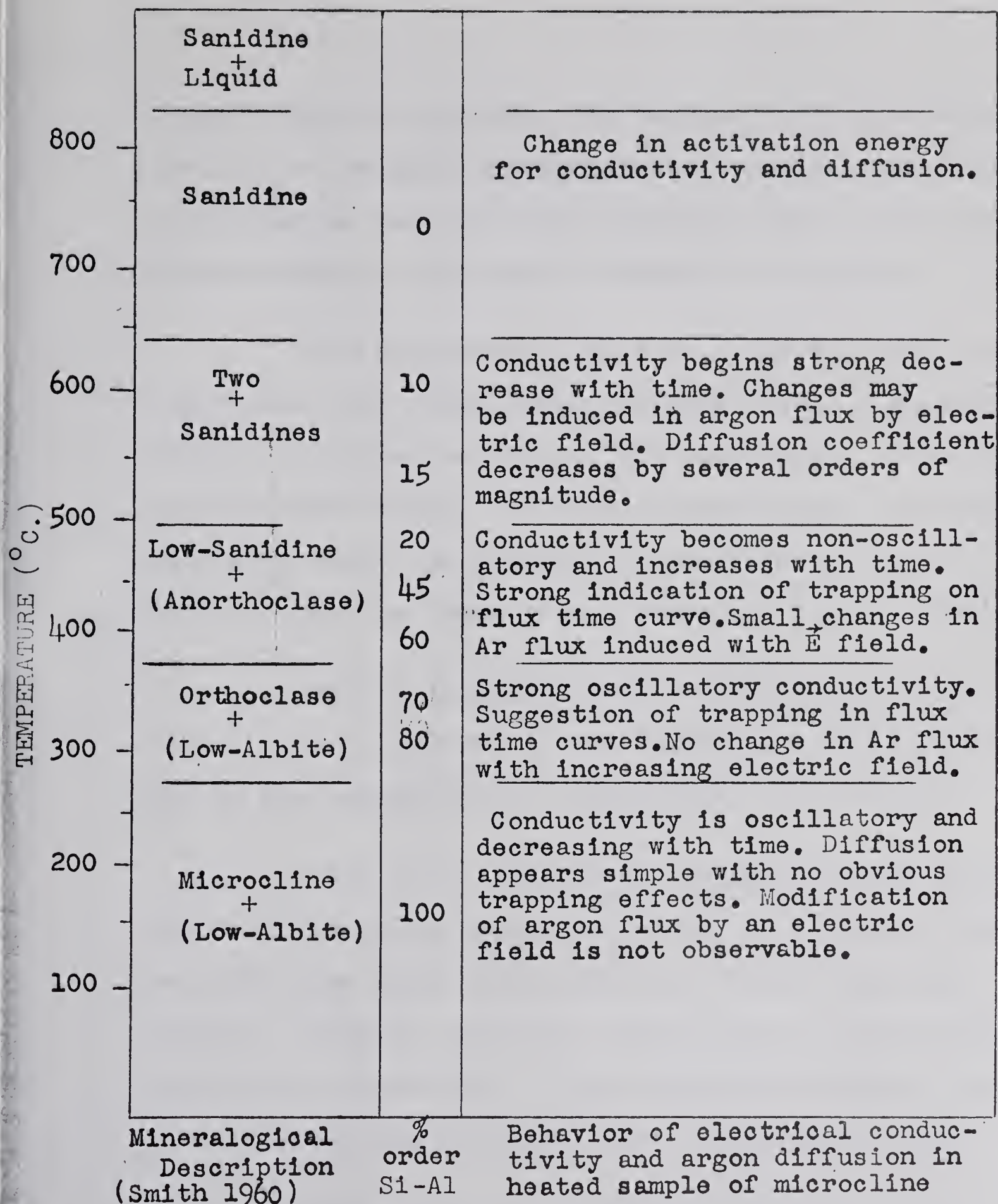


Figure VII-2. Qualitative description of transport properties in microcline as a function of disordering and temperature.

crystal of microcline upon slow heating, will show characteristics in its transport properties which indicate the presence of disordering and a general conversion over to the properties characteristic of the atomic transport in sanidine.

This conversion occurs on an atomic level and at a very slow rate, there being no gross visual changes associated with it during the time of the experiment. (i.e. the order of a few days). At higher temperatures, a visually observable change is possible as homogenization of the perthitic lamellae takes place [Bowen and Tuttle, 1950].

Obvious changes in the transport properties of microcline were observed at the temperature which these authors give as the homogenization temperature (i.e. 650°C).

Additional evidence for transformations occurring over the temperature range 400 to 650°C is seen in Figure VII-3. These data are taken from Lipson and Pronko [1962] and represent Arrhenius plots for conductivity of microcline, orthoclase, and sanidine. The temperature range is one which includes the effects of ionic conductivity only.

Microcline has a conductivity that is three orders in magnitude smaller than that of sanidine. This could be attributed to the absence of defects in microcline (which is

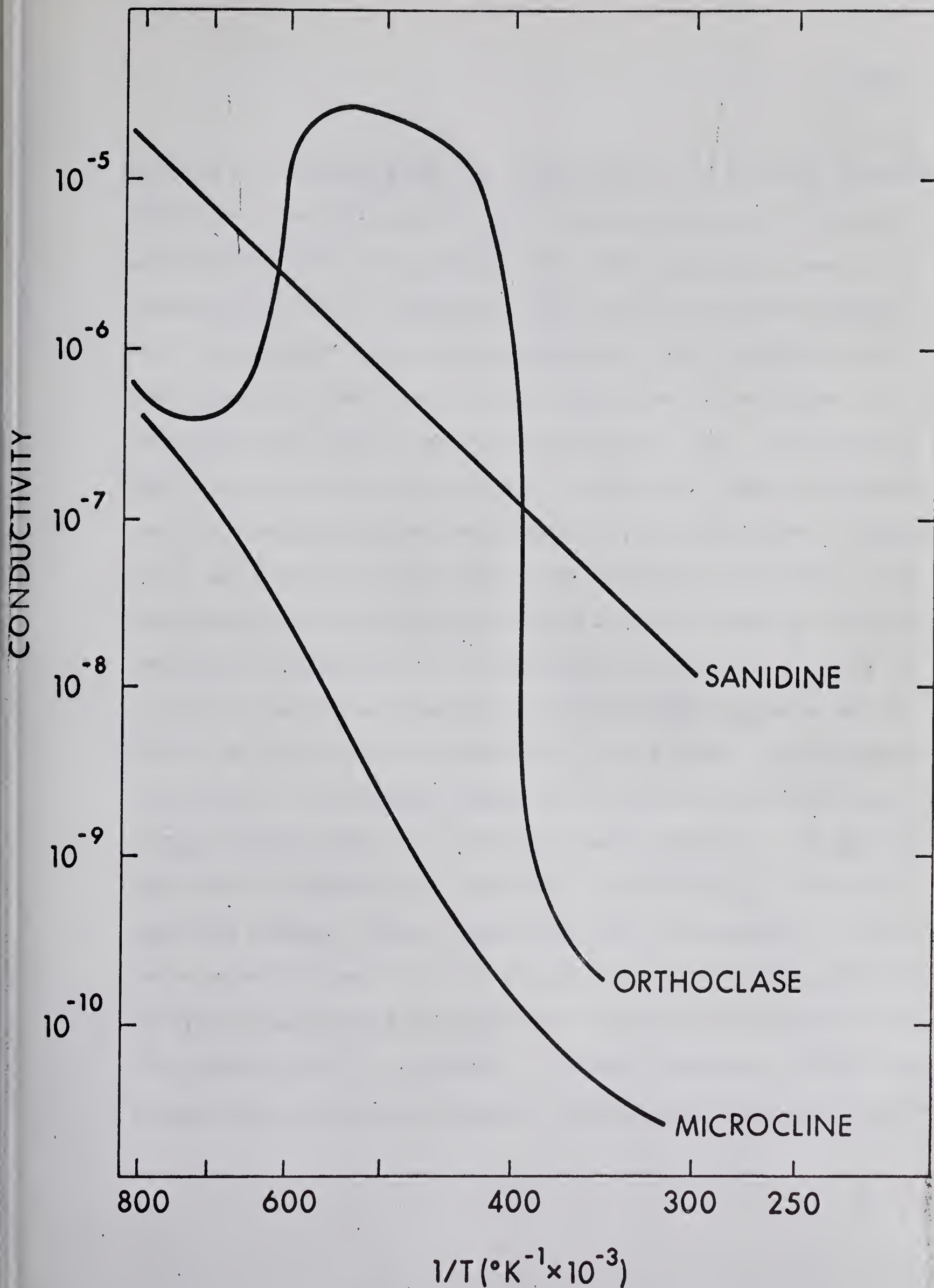


Figure VII-3. Arrhenius plots of conductivity for microcline, sanidine, and orthoclase.

ordered) as compared to the large density of defects quenched into disordered sanidine. Orthoclase generally occurs as an intermediate form between these two states and has a conductivity which undergoes a much more pronounced change with temperature than does microcline. This suggests that orthoclase is less stable than microcline or sanidine. It can be shown that microcline will exhibit the same kind of conductivity curve as orthoclase if sufficient time is allowed for the disordering and rearrangement to take place. Figure VII-4 demonstrates this effect as observed in run #66. The increasing and decreasing portions are due first to the disordering accompanied by the generation of vacancies (450°C to 600°C) and then possibly a recombination process which occurs as the lattice adjusts to the new state of disorder. This final re-adjustment might also be associated with the highly mobile state of perthitic homogenization. It will be observed in Figure VII-3 that the conductivity of sanidine does not undergo these transitions with temperature. This is attributed to the fact that sanidine is already disordered at the low temperatures and does not suffer these transitions as the temperature is increased. A single unaltered activation process is in effect throughout the entire temperature interval.

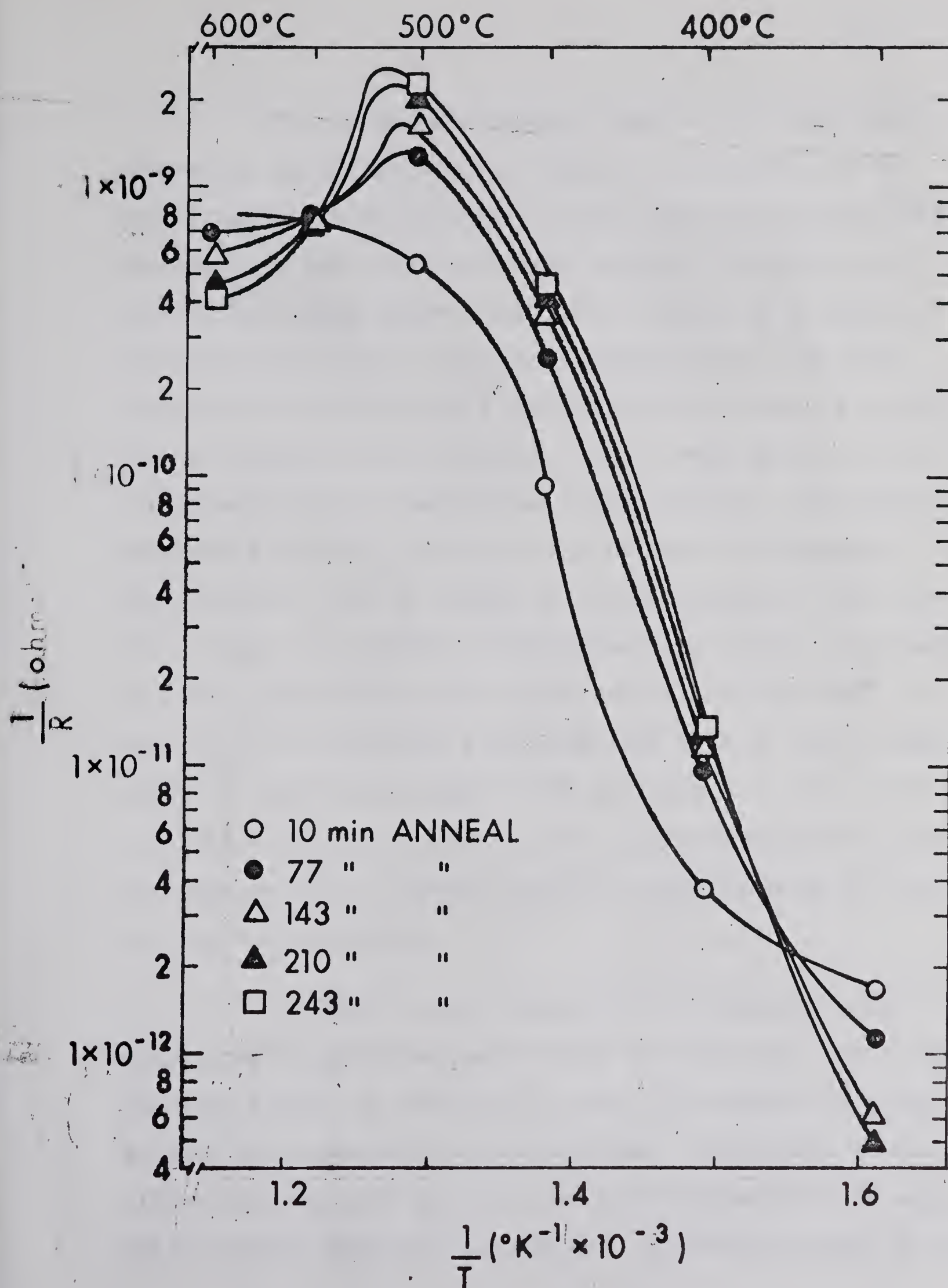


Figure VII-4. Time dependence of Arrhenius plot for microcline.

If the phase diagram of Smith is correct and reversible (given sufficient time for equilibrium to be established), it would appear on the basis of the quenched samples that the relative degree of Si-Al order does not control the twinning in microcline. Quenching a sample of microcline from 550°C does not visibly affect the twin structure or the perthitic exsolution, yet there is no doubt that a transition has occurred. It is well known that at sufficiently high temperatures (above 700°C), the perthitic exsolution and twin structure can be made to disappear. X-ray data however, show no change of crystal symmetry until the 700°C mark is reached. This means that either the disordering is not accomplished at the first transition near 450°C or else it is a transition involving some kind of short range order not observable under X-ray analysis. If this first transition does not represent Si-Al disordering, there is no alternative but to consider Smith's phase diagram as inaccurate or else non-reversible.

At 450°C , the diffusion coefficient of argon in microcline drops by several orders of magnitude. This large decrease occurs in conjunction with the creation of a high density of vacancies and dislocations. This seems anomalous since vacancies and dislocations are considered to be agencies which enhance diffusion in solids. Although this may be true

for self diffusion, it is not necessarily the case for impurity diffusion of inert gases. In view of the behavior exhibited by the "linearized" flux time curves (Figures IV-14, IV-15, and IV-16) and the $\ln V_{\max}$ vs. $1/T$ plots (Figures VII-1), a model employing atomic trapping of argon in vacancies or clusters of vacancies is appropriate. Not only does this explain the experimental evidence of the present work, but it also is in accord with observations of Baadsgaard et al [1961] on argon diffusion in sanidine and microcline and with Amirkhanoff [1961] on argon diffusion in sylvite (KCl). The latter observed a severe drop in diffusion coefficient near 550° C where the density of Shottky defects is known to increase sharply. The former investigators found that disordered sanidine had a diffusion coefficient which was several orders of magnitude smaller than ordered microcline.

The concepts of argon trapping in vacant lattice sites or dislocation voids also explains the so-called mica-feldspar discrepancy in argon retention. This is the situation where microcline and orthoclase appear to have lost as much as 40% of the radiogenic argon from its lattice over geologic time as compared to mica. Mica generally contains a large concentration of defects. These defects, largely in the form of vacancies, could supply the trapping sites for the retention of argon. Feldspar in the ordered state (i.e. microcline and

orthoclase) does not possess the large defect concentration and therefore would not be able to retain argon as well. A dense dislocation pattern associated with the above effect could completely account for the high loss of argon from microcline.

APPENDIX I.

TRANSFORMATION OF DOUBLY BOUNDED REGION TO A SINGLY BOUNDED REGION

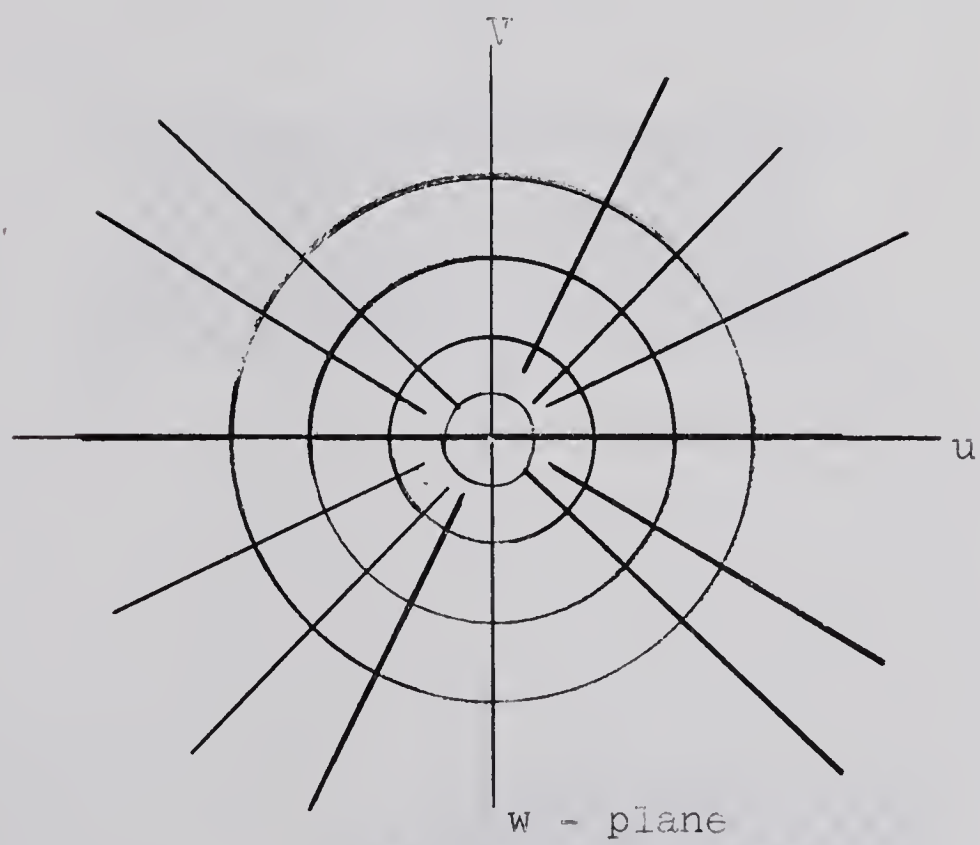
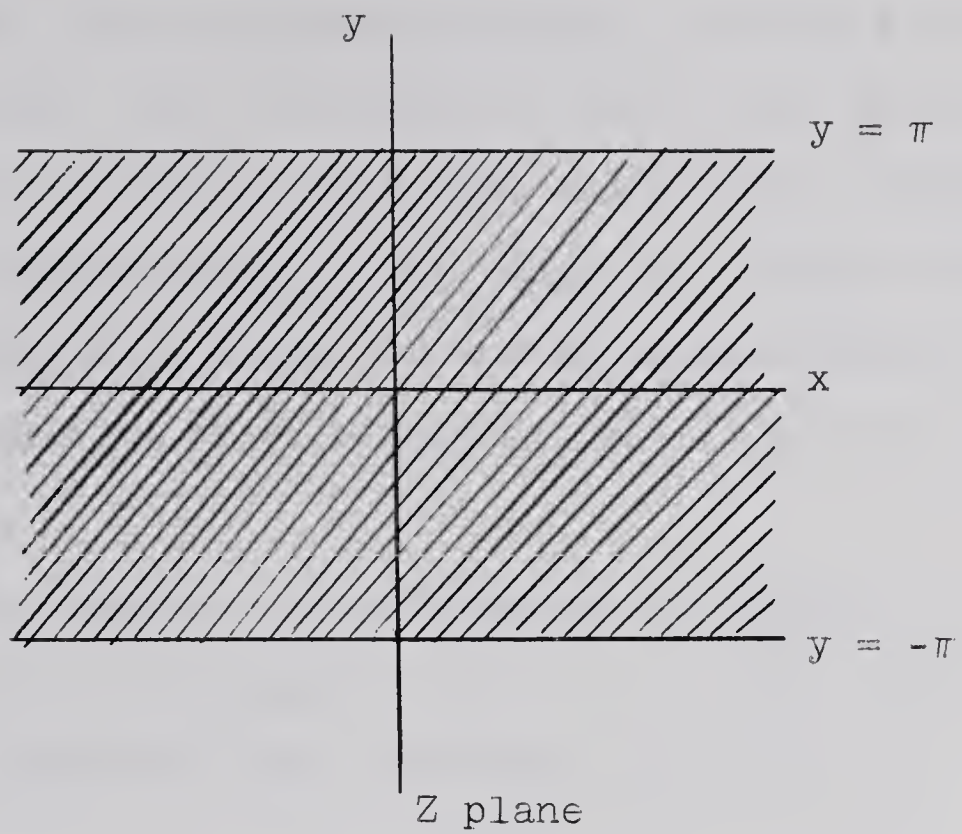
As discussed in Chapter III, the Green's function for a doubly bounded region is an infinite series, whereas it is very simple for a singly bounded region. Because of this, the double boundaries of a thin slab have been converted to a single boundary surface by the methods of conformal mapping. The development of Chapter III uses Fig. 6 Appendix II of Churchill [1960] as a guide. This is a specialized version of the Schwartz transformation discussed by Franklin [1944] P. 240.

The Z plane and the w plane are both complex number planes, Z being defined as $Z = x + iy$ and w being defined as $w = u + iv$. The objective is to transform a given geometry of the Z plane to one which is mathematically easier to handle in the w plane. The functional connection between the Z and w plane will be $Z = \text{Log } w$, or $w = e^Z$.

$$\text{Let } Z = x + iy = \text{Log } w \qquad w = e^Z = u + iv$$

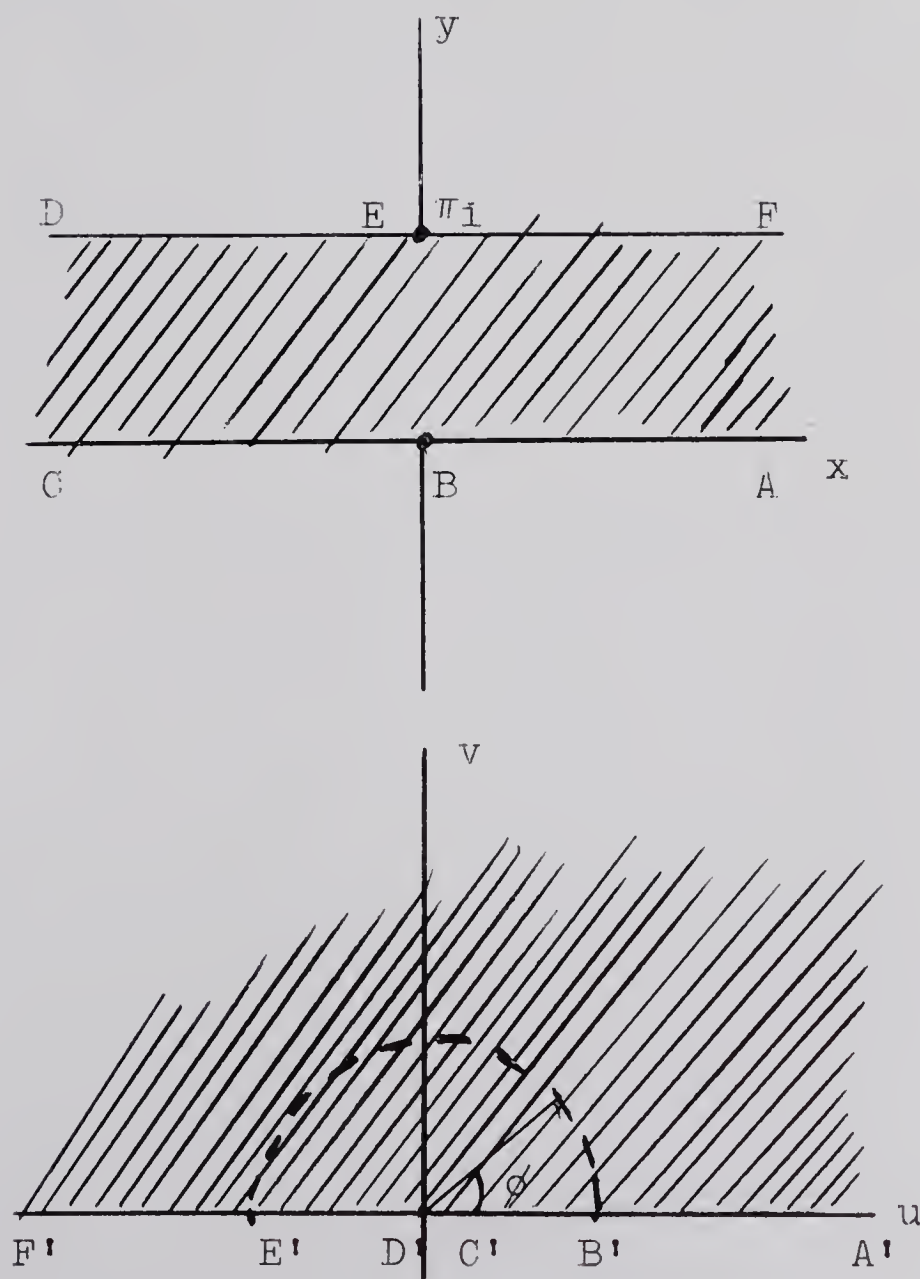
This maps the region between $y = 0$ and $y = \pi$ of the Z plane to the upper half w plane, and the region between $y = 0$ and $y = -\pi$ of the Z plane to the lower half w plane.

A2.



The transformed lines of $x = \text{constant}$ are concentric circles in the w plane and the transformed lines $y = \text{constant}$ are straight lines through the origin of the w plane. These straight lines through the origin will be oriented with respect to the $+u$ axis with values of ϕ ranging from $-\pi$ to $+\pi$ corresponding to the range of y values from $-\pi$ to $+\pi$. This geometry will allow for any arbitrary initial distribution since integration of Eq.III-13 is carried out over the entire range of ϕ .

The choice of co-ordinates of Chapter III was such as to restrict y to values $0 \leq y \leq \pi$. This results in the following geometry. (The coordinate of B are $0,0$).



The initial distribution in the x, y plane is converted to the u, v plane. If this is chosen as $\psi = C_0 \sin y$ in the x, y plane, it goes over to $\psi_0 = C_0 \sin \phi$.

$$e^{x+iy} = u + iv$$

$$e^x e^{iy} = e^x (\cos y + i \sin y) = u + iv$$

$$\text{Chose } x = 0$$

$$\text{Then } u = \cos y$$

$$v = \sin y$$

Also

$$e^x e^{iy} = u + iv = \rho e^{i\phi}$$

$$\rho = e^x = 1 \text{ if } x = 0$$

$$e^{i\phi} = e^{iy}$$

$$\therefore y = \phi, \rho = 1.$$

Appendix II

EVALUATION OF THE CONTOUR INTEGRAL OF EQUATION III-13.

Using an initial distribution in the u, v plane of $\psi_{ow} = C_o \sin \varphi_o$ the integral of equation III-13 becomes:

$$I = \int_0^{\pi} \sin \varphi_o e^{K \cos \varphi_o} \sinh (\delta \sin \varphi_o) d\varphi_o \quad \text{AII-1}$$

The integrand is an even function of φ_o so that the limits of integration may be changed as follows:

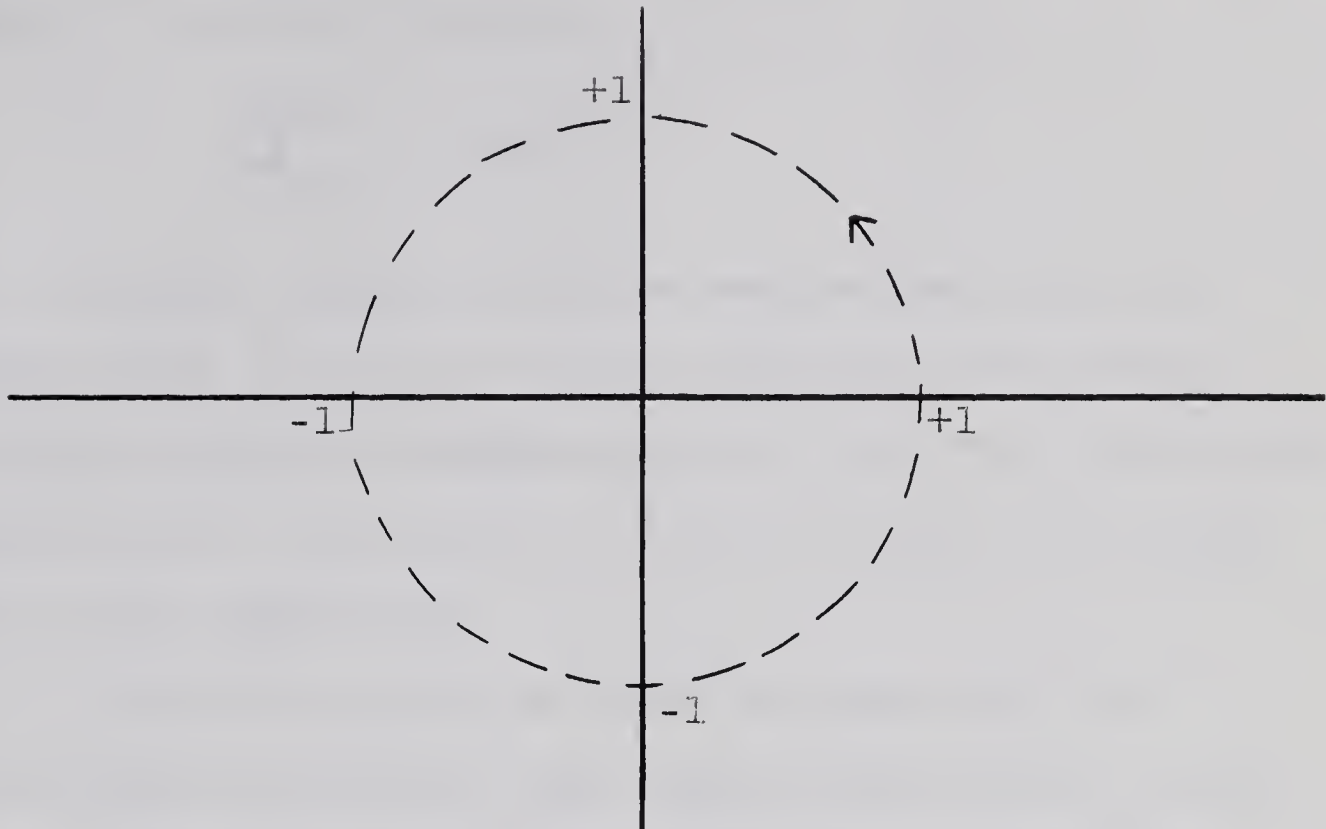
$$I = \frac{1}{2} \int_0^{2\pi} \sin \varphi_o e^{K \cos \varphi_o} \sinh (\delta \sin \varphi_o) d\varphi_o \quad \text{AII-2}$$

In order to evaluate this integral, make the transformation

$$Z = e^{i\varphi_o} \quad \text{or} \quad i\varphi_o = \ln Z \quad \text{AII-3}$$

when φ_o moves through values 0 to 2π , Z traverses a unit circle [Franklin, 1944; pp.220 & 240]

Contour of Integration in the Z plane.



The Cauchy Residue Theorem may be applied in evaluating the integral

$$I = -\frac{1}{4} \int_c \frac{(z^2-1)}{z^2} e^{K(\frac{z^2+1}{2z})} \sinh\left(\frac{z^2-1}{2iz}\right) dz \quad \text{AII-4}$$

The symbol $\int_c$ represents line integration over the contour of the unit circle. According to the Cauchy Residue Theorem, this will be

$$I = -\frac{1}{4}(2\pi i)R_0 \quad \text{AII-5}$$

where R_0 is the residue of the isolated essential singularity at the origin. This reduces the problem of evaluating the

integral to a determination of the residue.

Let the integrand be represented by $f(Z)$. Then according to Laurent's Theorem,

$$f(Z) = \sum_{-\infty}^{\infty} a_n (Z-a)^n$$

$f(Z)$ is a regular analytic function everywhere except at the origin where it has an isolated essential singularity. This singular point is represented by $a = 0$. The coefficient a_{-1} (which is the coefficient of $1/Z$) is called the residue of $F(Z)$ at the singularity.

Further details of these theorems and their application may be obtained from Copson [1935, Chap. IV,V].

The calculation of the residue at the origin requires that a Laurent expansion of the integrand be made and the coefficient of the term $1/Z$ determined. This can be easily accomplished by using the power series expansions for the exponential and Sinh terms. These expansions are then multiplied in the appropriate fashions so that they represent the complete integrand. The steps required to obtain the coefficient of $1/Z$ are simple enough to follow; however, carrying them out can be very cumbersome. Only the pertinent details of this calculation will be included here. The necessary terms involved will be listed for the sake of completeness and for reference purposes if the calculation for

other distributions are required.

The power series expansion for the Sinh term is

$$\text{Sinh}\left(\frac{Z^2-1}{2iZ}\right) = \delta\left(\frac{Z^2-1}{2iZ}\right) + \frac{\delta^3}{3!} \left(\frac{Z^2-1}{2iZ}\right)^3 + \frac{\delta^5}{5!} \left(\frac{Z^2-1}{2iZ}\right)^5 + \frac{\delta^7}{7!} \left(\frac{Z^2-1}{2iZ}\right)^7 + \dots$$

AII-7

The power series expansion for the exponential is

$$\begin{aligned} e^{k\left(\frac{Z^2+1}{2Z}\right)} &= 1 + \frac{k}{2Z}(Z^2+1) + \frac{k^2}{2!} \frac{1}{2^2 Z^2} (Z^2+1)^2 + \frac{k^3}{3!} \frac{1}{2^3 Z^3} (Z^2+1)^3 \\ &+ \frac{k^4}{4!} \frac{1}{2^4 Z^4} (Z^2+1)^4 + \frac{k^5}{5!} \frac{1}{2^5 Z^5} (Z^2+1)^5 + \frac{k^6}{6!} \frac{1}{2^6 Z^6} (Z^2+1)^6 \\ &+ \frac{k^7}{7!} \frac{1}{2^7 Z^7} (Z^2+1)^7 + \frac{k^8}{8!} \frac{1}{2^8 Z^8} (Z^2+1)^8 + \frac{k^9}{9!} \frac{1}{2^9 Z^9} (Z^2+1)^9 + \dots \end{aligned}$$

AII-8

The complete integrand is given as

$$K = \frac{Z^2-1}{Z^2} e^{k\left(\frac{Z^2-1}{2Z}\right)} \text{Sinh}\left(\delta \frac{Z^2-1}{2iZ}\right) \quad \text{AII-9}$$

Write the expansion for Sinh as

$$\text{Sinh}\left(\delta \frac{Z^2-1}{2iZ}\right) = \delta\left(\frac{Z^2-1}{2iZ}\right) + \sum_{m=2}^{\infty} \delta^m g^m(Z) \quad \text{AII-10}$$

then k becomes

$$\left[\delta \left(\frac{Z^2-1}{2iZ} \right) \frac{Z^2-1}{Z^2} + \frac{Z^2-1}{Z^2} \sum_{m=2}^{\infty} \delta^m g^1(Z) \right] e^{k \left(\frac{Z^2+1}{2Z} \right)} \quad \text{AII-11}$$

or

$$K = \left[\frac{\delta}{2i} \left(Z - \frac{2}{Z} + \frac{1}{Z^3} \right) + \sum_{m=2}^{\infty} \delta^m g(Z) \right] e^{k \left(\frac{Z^2+1}{2Z} \right)} \quad \text{AII-12}$$

Let

$$\left[\sum_{m=2}^{\infty} \delta^m g(Z) \right] e^{k \left(\frac{Z^2+1}{2Z} \right)} = W \quad \text{AII-13}$$

Then

$$K = \frac{\delta}{2i} \left(Z - \frac{2}{Z} + \frac{1}{Z^3} \right) e^{k \left(\frac{Z^2+1}{2Z} \right)} + W \quad \text{AII-14}$$

where expansion AII-8 is to be substituted for the exponential term.

This will result in a series expansion for K which will contain powers of Z and powers of 1/Z. This is the Laurent expansion of the integrand.

Collecting terms in 1/Z results in a determination of its coefficient and hence the residue.

Adding up the terms which comprise the coefficients of 1/Z results in

$$-\frac{\delta}{iZ} - \frac{\delta}{2iZ} \left\{ \frac{2K^2}{2!2^2} + \frac{4K^4}{4!2^4} + \frac{10K^6}{6!2^6} + \frac{28K^8}{8!2^8} + \frac{84K^{10}}{10!2^{10}} + \frac{234K^{12}}{12!2^{12}} + \dots \right\} \\ + \sum_{m=2}^{\infty} \delta^m F(K)$$

This is the residue R_0

$$\text{Let } \sum_{m=2}^{\infty} \delta^m F(K) = W'$$

W' is a term which contains sums of products of higher order values of δ such as δ^2 , δ^3 , etc. These will all be grouped together as W' and their effect shown to be identically zero in the final determination of the flux at the surface of the crystal.

Rearranging the terms of AII-15 gives the residue R_0 as:-

$$R_0 = -\frac{\delta}{2i} \left\{ 2 + (0.5) \frac{K^2}{2!} + (0.25) \frac{K^4}{4!} + (0.156) \frac{K^6}{6!} + (0.109) \frac{K^8}{8!} + (.082) \frac{K^{10}}{10!} + (.057) \frac{K^{12}}{12!} + \dots \right\} + W' \quad \text{AII-16}$$

This series can be very closely approximated by a hyperbolic cosine.

$$\cosh x = 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + \frac{x^6}{6!} + \dots \quad \text{AII-17}$$

It is necessary to supply a quantity in the argument which will result in the appropriate coefficients of the expansion terms.

It is found that the series for R_0 is very closely

approximated by

$$R_0 \approx - \frac{\delta}{2i} \frac{1}{Z} \left\{ 1.51 + (.7)^2 \cosh(\sqrt{.7} K) \right\} + W' \quad \text{AII-18}$$

The following is a comparison of the coefficients for the various powers of K in AII-16 and AII-18

Power of K	0	2	4	6	8	10	12	
Exact value	2	0.50	0.25	0.156	0.109	.082	.057	
Approx. value	2	0.343	0.24	0.168	0.117	.082	.057	

Except for the 2nd power of K, the agreement is very good and the approximation of series AII-16 by equation AII-18 will be used.

This completes the calculations of the residue R_0 .

The integral III-13 which we set out to determine will then be given by.

$$I = - \frac{1}{4} [2\pi i] R_0$$

Or

$$I = \frac{\delta\pi}{4} \left\{ 1.51 + (.7)^2 \cosh(\sqrt{.7} K) \right\} + W' \quad \text{AII-19}$$

This completes the calculation of integral III-13 in the sense that all necessary terms (for our present purpose) have been determined.

APPENDIX III.

Evaluation of Flux-Time Equation at Surface of Crystal.

As shown in Appendix II,

$$I \simeq \frac{\delta\pi}{4} \left\{ 1.51 + (.49) \cosh(\sqrt{.7} K) \right\} + W' \quad \text{AIII-14}$$

Therefore, equation III-12 becomes

$$\psi = \frac{C_0 A}{\tau} e^{-\frac{\alpha}{2} (\rho^2 + \rho_0^2)} \left[\frac{\delta\pi}{4} \left\{ 1.51 + (.49) \cosh(\sqrt{.7} K) \right\} + W' \right]$$

ψ and C_0 have units of atoms per radian since the equation represents the concentration in the U, V plane. It is preferable to convert this equation to the complex crystal plane before calculating the flux at the surface of the crystal. This will put the results in a more physically obvious form. ψ is the concentration of diffusing substance as a function of position and time. In order to determine the flux at the surface of the crystal, one makes the appropriate conversion back to the complex ξ plane and then takes the negative gradient of ψ according to Fick's law $F = -D\nabla\psi$

$$\nabla\psi = \cancel{\frac{\partial\psi}{\partial x} \vec{i}}^0 + \frac{\partial\psi}{\partial y} \vec{j} + \cancel{\frac{\partial\psi}{\partial z} \vec{k}}^0$$

Converting to the U,V plane $\phi \rightarrow y$, $\rho \rightarrow 1$. Evaluating the flux at the surface of the crystal corresponds to $y = 0$, π , $\rho = 1$.

The important thing to notice at this stage is the positioning of δ and w' . The original expansion and grouping of terms for the integrand was done in such a way that they would appear in the positions which they occupy..

$$\delta = \alpha \gamma \rho \rho_0 = \frac{a^2}{2\tau} \sin \phi$$

$w' =$ sums of higher powers of δ .

Taking the negative gradient of ψ and evaluating it at the surface of the crystal results in all w' derivatives being zero. There will be only one non-zero term in the entire expression for the flux. This is the first term which is multiplied by δ .

The results of this give the flux at the surface of the crystal as

$$F = \left(\frac{DA\pi C_0}{4} \right) \left(\frac{a^2}{2\tau^2} \right) e^{-a^2(\rho^2 + \rho_0^2)/4\tau} (\rho \rho_0 \cos \phi) \left\{ 1.51 + (.49) \right. \\ \left. \cosh(\sqrt{.7} K) \right\} \bigg|_{\substack{\rho_0 = \rho = 1 \\ \phi = \pi}}^{\substack{\rho_0 = \rho = 1 \\ \phi = 0}}$$

When converting this to the real crystal plane (i.e. the x, y plane), it is important to remember that the numerical value of 1 in the complex ξ plane is equal to ℓ/π in the

x,y plane. Therefore $\rho = 1$ must be written as l/π in the real crystal wafer.. Also $\cos \phi \Big|_{\phi=0} = 1$ must be written as l/π in the real crystal coordinate system.

This gives for the flux at the surface of the real crystal .

$$F = \frac{C_o DA}{4\rho} \frac{a^2 l^3}{\pi^3} \frac{e^{-\frac{a^2 l^2}{2\pi^2 \tau}}}{\tau^2} \left\{ 1.51 + (.49) \cosh (\sqrt{.7} K') \right\}$$

$$a^2 = \frac{1}{D} \quad A = \frac{a^2}{4\pi} = \frac{1}{4\pi D}$$

$$K' = \alpha \rho \rho_o = \frac{l^2}{\pi^2} \frac{a^2}{2\tau} = \frac{l^2}{2\pi^2 D \tau}$$

$$|F| = C_o \left(\frac{l}{2\pi}\right)^2 \frac{l}{\pi D} \frac{e^{-\frac{l^2}{2\pi^2 D \tau}}}{\tau^2} \left\{ 1.51 + (.49) \cosh \left(\sqrt{.7} \frac{l^2}{2\pi^2 D \tau} \right) \right\}$$

C_o = maximum value of original concentration

l = thickness of the crystal slab

D = diffusion coefficient

τ = time

F = flux at surface in atoms/sec

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